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Solving the Challenging Synthesis of Highly Cytotoxic Silver Complexes bearing Sterically Hindered NHC Ligands with Mechanochemistry

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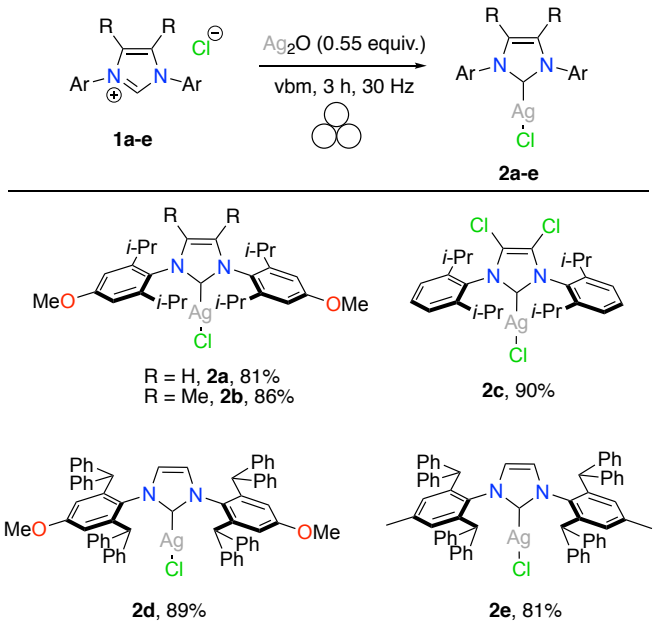
Abstract. The use of ball-mills enabled the straightforward synthesis of a variety of silver(I) complexes featuring challenging NHC ligands. Sterically hindered including electron-poor or with very low solubility imidazolium salts were grinded with silver(I) oxide to furnish heteroleptic or homoleptic complexes in high yield and short reaction times. The synthesis of heteroleptic bis-NHC silver(I) complexes was also performed for the first time in a ball-mill. The efficiency and rapidity of the mechanochemical approach enabled the generation of a library of unprecedented NHC silver complexes, which cytotoxicity on HCT116 colorectal cancer cell line was evaluated providing a rare example of medicinal mechanochemistry. The cationic silver complexes were found more potent than the neutral analogues, with IC_{50} values down to 21 nM, 256 times more potent than cisplatin.

N-heterocyclic carbenes (NHC) are widely used for the stabilization of transition metals, especially compared to phosphines in catalytic systems.[1] Additionally, NHC-based complexes have found interest due to their biological properties, for example for their antibacterial, antifungal or anticancer properties.[2] Besides, many groups have shown that NHC-gold(I) and NHC-gold(III) complexes could be valid alternatives to cisplatin due to their different mode of action.[3] Silver(I) complexes have also been studied because they might behave similarly to gold complexes.[2a-e, 4] However, NHC-silver(I) complexes have mostly been studied for their antibacterial and antimicrobial activity,[5] and only some of them were found to be active as anticancer agents.[6] However, most of these complexes were either neutral [AgCl(NHC)] complexes or cationic homoleptic [Ag(NHC)$_2$] complexes featuring *N*,*N*-dialkyl ligands. Cationic homoleptic [Ag(NHC)$_2$] complexes bearing *N*,*N*-diaryl NHC ligands have been less studied because their synthesis is known to be more challenging. Yet, we recently developed a mechanochemical[7] solvent-free method that enables a rapid and highly efficient access to such complexes.[8] Additionally, ball-milling permits to easily synthesize neutral [AgCl(NHC)] complexes, either with alkyl or aryl substituents.[9] In this manuscript, we initially focused our attention on the mechanosynthesis of less conventional silver complexes bearing sterically hindered NHC including one with electron withdrawing groups, to assess if the mechanochemical approach could solve synthetic problems encountered in solution.[7d] Then, we evaluated the cytotoxicity of the corresponding complexes, as well as heteroleptic bis-NHC complexes, as anticancer agents on colorectal HCT116 cancer cell line. Of note, this represents one of the rare examples of mechanochemical synthesis of molecules for biological testing, a branch of medicinal mechanochemistry.[10]

First, the synthesis of neutral heteroleptic complexes was realized by milling highly encumbered imidazolium salts **1a-e** and silver(I) oxide in slight excess in a stainless steel jar containing a 1 cm diameter stainless steel ball, using a vibratory MM400 ball-mill (Scheme 1). Gratifyingly, after 3 h at 30 Hz, full conversion was obtained in all cases. Complexes **2a** and **2b**, featuring ligands IPr^{OMe} (1,3-bis(4-methoxy-2,6-di*iso*propylphenyl)imidazol-2-ylidene) and ^{Me}IPr^{OMe} (1,3-bis(4-methoxy-2,6-di*iso*propylphenyl)-4,5-dimethylimidazol-2-ylidene) could be isolated in 81% and 86% yield, respectively. In solution, the use of electron poor ^{Cl}IPr·HCl **1c** (1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloroimidazolium chloride)

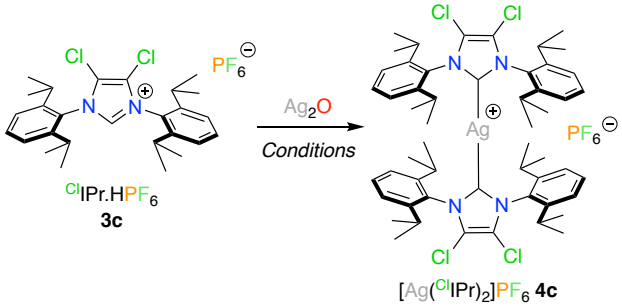


Scheme 1. Mechanosynthesis of [AgCl(NHC)] complexes bearing highly encumbered NHC ligands

revealed problematic. Indeed, even when full conversion was obtained, isolated yield of corresponding complex **2c** did not exceed 31%.[11] Of note, the same trend was observed in the synthesis of [CuCl(ClIPr)], with 40% being the highest reported isolated yield.[12] Using the ball-mill, full conversion of **1c** was also observed, but, in sharp contrast to the solution, upon treatment, complex **2c** was isolated in an excellent 90% yield. Increased steric hindrance was not a limit to the method as complexes **2d** and **2e**, featuring IPr*OMe ([1,3-bis(4-methoxy-2,6-diphenylmethyl)phenyl]imidazol-2-ylidene)[13] and IPr* ([1,3-bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazol-2-ylidene)[14] ligands, were isolated in 89% and 81%, respectively. It is important to highlight that the solvent-free method revealed highly practical in these cases since the imidazolium salts **1d** and **1e** are poorly soluble in organic solvents and water.

We then turned our attention to unprecedented homoleptic $[Ag(NHC)_2]PF_6$ complexes. Imidazolium salts **1a-i** were first converted into their PF_6 counterpart **3a-i** using either the classical method, which consists in solubilizing the chloride salt in water in the presence of KPF_6 and recover the hexafluorophosphate salt that precipitates, or our previously reported solvent-free milling approach.[8]

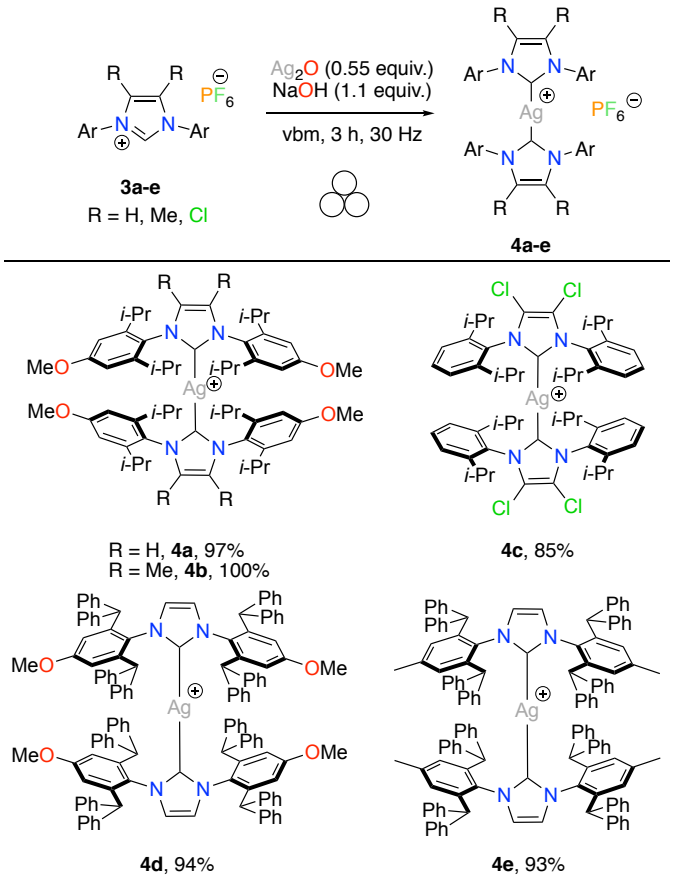
Table 1. Comparison of methods for the synthesis of $[Ag(^{Cl}IPr)_2]PF_6$.[a]



Entry	Conditions	t (h)	Conv. (%)[b]
1	$CHCl_3$, reflux	24	31
		48	90
2	NaOH (1.1), CH_2Cl_2, rt	24	100 (45)
3	NaOH (1.1), vbm, 30 Hz	3	100 (85)

[a] Reaction conditions: **3c** (0.15 mmol, 1 eq.), Ag_2O (0.075 mmol, 0.5 eq.). [b] Conversion determined by ^1H NMR. Isolated yield is given in brackets.

This latter technique enabled the reduction of the quantity of KPF_6 and water used, and was found to be particularly efficient for salt **1e** that reacts poorly in water due a reduced solubility. In the ball-mill, anion metathesis occurred in 30 min under solvent-free conditions. We first focused on the synthesis of complex **4c**, featuring electron poor ClIPr ligand (Table 1). As discussed above, isolation of complexes featuring this ligand is difficult when the reaction is performed in solution. Reaction of **3c** with silver(I) oxide in refluxing chloroform gave only 31% NMR conversion after 24h, and 90% after 48h (Table 1, entry 1). In dichloromethane at room temperature, with the addition of sodium hydroxide, it was possible to obtain full conversion of ClIPr·HPF_6 **3c** in 24 h (Table 1, entry 2). However, upon isolation through filtration on Celite® and evaporation, complex **4c** was obtained in only 45% yield. When imidazolium salt **3c** was ball-milled with NaOH and Ag_2O under solvent-free conditions at 30 Hz for 3h, 100% conversion was also observed. More importantly, after the same treatment as when the reaction was performed in solution, homoleptic complex $[Ag(^{Cl}IPr)_2]PF_6$ **4c** was isolated in 85% yield (Table 1, entry 3). The desired complex **4c** may thus easily decompose in solution while the solvent-free approach gives a much faster access the complex and in a two-fold higher isolated yield.



Scheme 2. Mechanosynthesis of homoleptic $[Ag(NHC)_2]PF_6$ complexes bearing highly encumbered NHC ligands

The mechanochemical approach was then applied to salts **3a-e** in the presence of silver oxide and sodium hydroxide (Scheme 2). As for complexes **2a-e**, full conversion was observed in all cases in 3 h of milling. Homoleptic complexes **4a** and **4b** were isolated in excellent yields. The milling method was then applied successfully to poorly soluble IPr*^{OMe}.HPF_6 **3d**. After 3h

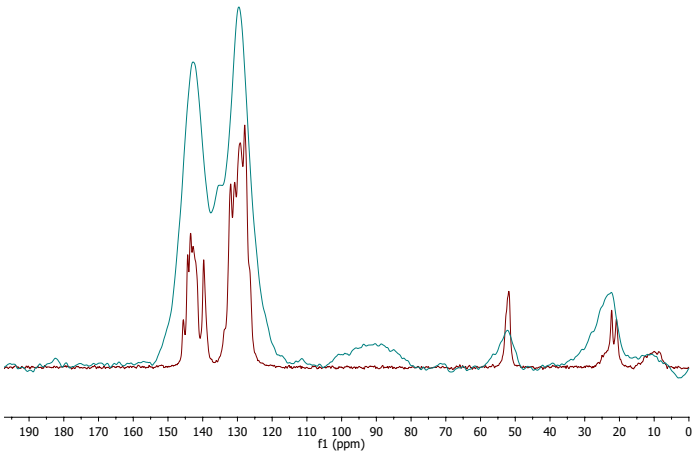
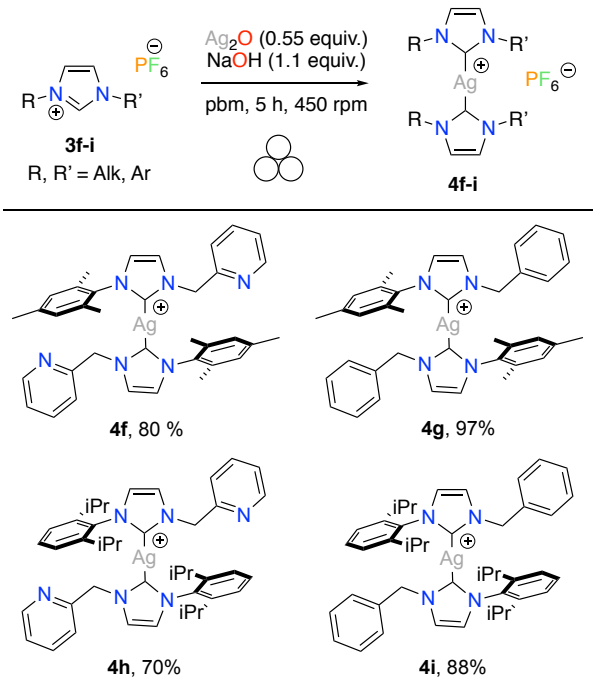


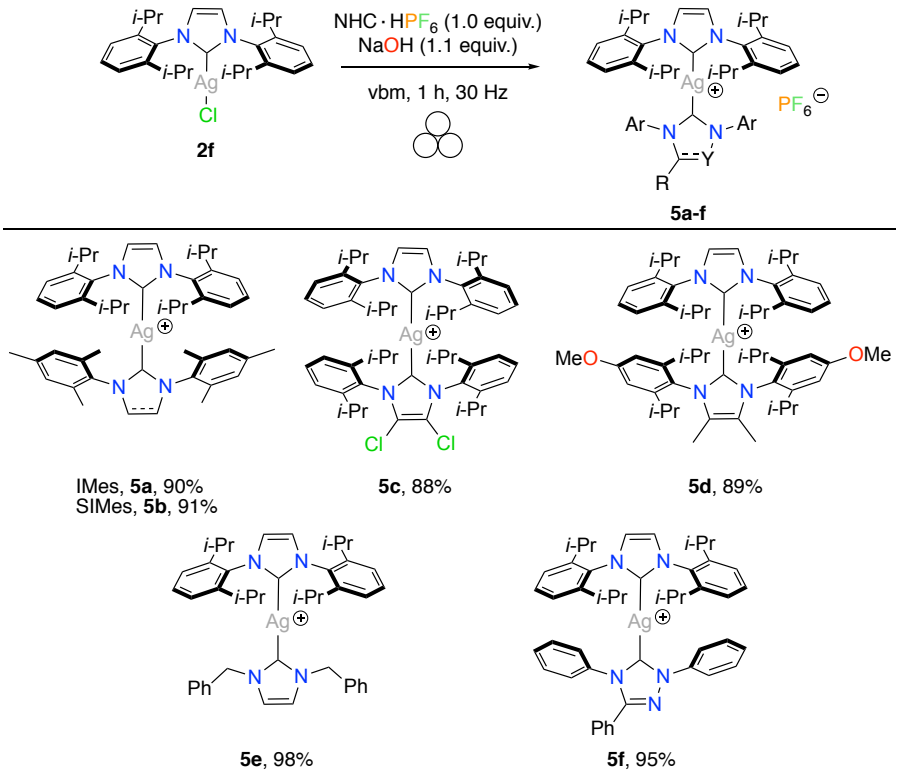
Figure 1. ^{13}C solid state HR-MAS NMR of IPr*.HPF_6 **3e** (red) and $[Ag(IPr^*)_2]PF_6$ **4e** (blue)



Scheme 3. Mechanosynthesis of homoleptic $[Ag(NHC)_2]PF_6$ complexes bearing *N*-alkyl, *N*-aryl ligands

of milling at 30 Hz, corresponding $[Ag(IPr^{*OMe})_2]PF_6$ **4d** was isolated in 94% yield. On the other hand, $[Ag(IPr^*)_2]PF_6$ **4e** revealed highly unstable compared to **4d**, probably because of the worse σ-donation of IPr* compared to IPr*^{OMe}. [13, 15] ^1H NMR analysis showed the disappearance of the characteristic C-H proton of the imidazolium salt **3e**, with the formation of corresponding complex **4e**. Due to a quick decomposition of **4e**, it was impossible to obtain ^{13}C NMR analysis of the pure compound.[16] Nevertheless, solid-state HR-MAS (high resolution magic angle spinning) ^{13}C NMR spectroscopy on a 600 MHz spectrometer confirmed the formation of the complex with the appearance of the characteristic carbenic carbon signal of **4e** at 182 ppm (Figure 1). The low stability of $[Ag(IPr^*)_2]PF_6$ **4e** could explain the low yields when the reactions were performed in solution. Indeed, the best conversion obtained when the reaction was attempted in refluxing chloroform was 62% after 48 h, yet along with important decomposition.[16] Comparatively, complex **4e** was isolated in 93% yield after 3h of milling.

The synthesis of novel homoleptic complexes featuring *N*-alkyl, *N*-aryl ligands was next performed (Scheme 3). Reaction of imidazolium salt **3f**, bearing a mesityl and a 2-picolyl group on the nitrogen atoms, was found to be slightly slower than with *N*,*N*-diaryl imidazolium



Scheme 4. Mechanosynthesis of cationic heteroleptic silver complexes

salts **3a-e**, with 79% conversion after 3 h at 30 Hz. Hence, reaction was performed using a planetary ball-mill, which is more adapted to longer reaction times. After 5 h at 450 rpm, full conversion was obtained, yielding complex **4f** in 80%. With a similar ligand bearing a benzyl instead of the 2-picolyl group, reaction proceeded efficiently and **4g** was isolated in 97% yield. Increasing the steric hindrance on the aromatic ring with a 2,6-diisopropylphenyl group resulted in slightly lower yields of 70% and 88% for **4h** and **4i**, respectively.

Finally, heteroleptic bis-NHC silver(I) complexes were synthesized using the vibratory ball-mill, starting from [AgCl(IPr)] **2f** (IPr = 1,3-bis(2,6-di*iso*propylphenyl)-imidazol-2-ylidene), which was prepared via mechanochemistry.[9a] To the best of our knowledge, the synthesis of heteroleptic silver(I) complexes was never attempted in a ball-mill. Reaction was thus first realized using classical IMes·HPF_6 (1,3-bis(2,4,6-trimethylphenyl)imidazolium) and SIMes·HPF_6 (1,3-bis(2,4,6-trimethylphenyl)imidazolinium) salts in the presence of sodium hydroxide (Scheme 4). After 1 h of milling at 30 Hz in a vibratory ball-mill, full conversions were obtained and heteroleptic complexes **5a** and **5b** were isolated in 90% and 91% yield, respectively. Reaction with ^{Cl}IPr·HPF_6 **3c** and ^{Me}IPr^{OMe}·HPF_6 **3b** yielded corresponding complexes **5c** and **5d** in 88% and 89%, respectively. To widen the scope of attainable heteroleptic complexes using this methodology, *N*,*N*-dibenzylimidazolium

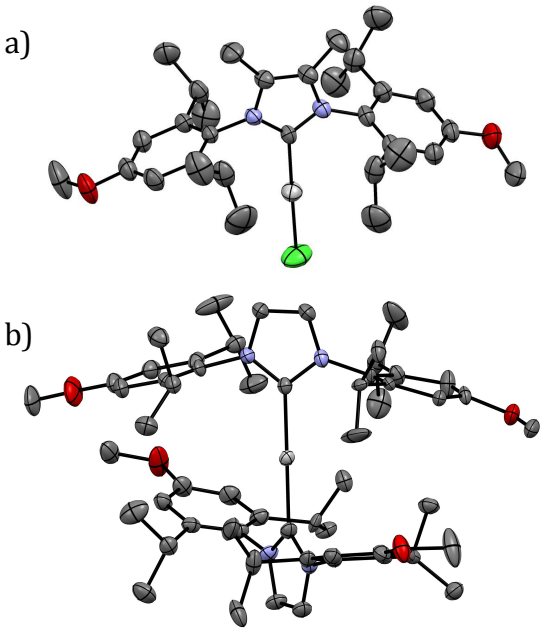


Figure 2. ORTEPs (at 50% probability level) of compounds (a) **2b**, (b) **4a**. Hydrogen atoms and PF_6 anion are omitted for clarity.

Table 2. $\%V_{bur}$ for the different complexes

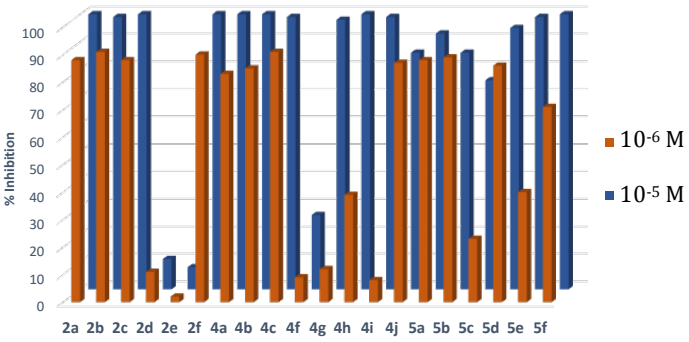
Entry	Complex	$d_{C\text{-}M}$ (Å)	%Vbur[a]	%Vbur[b]
1	**2a**	2.080	40.2	41.3
2	**2b**	2.087	42.8	42.5
3	**2e**[14]	2.078	52.9	52.9
4	**4a**	2.099	38.7	38.7
5	**4b**	2.122	40.2	40.7

[a] %Vbur calculated with real C-Ag distance, sphere radius of 3.5 Å. [b] distance C-Ag normalized at 2.1 Å, sphere radius 3.5 Å.

hexafluorophosphate and TPT·HPF_6 (1,3,4-triphenyl-1,2,4-triazolium hexafluorophosphate) were reacted efficiently to furnish **5e** and **5f** in excellent yields. X-ray quality crystals could be grown by slow diffusion of diethyl ether into a dichloromethane solution of complexes **2a**, **2b**, **4a** and **4b** (Figure 2). XRD analysis allowed to evaluate the steric properties of the ligands by calculating the $\%V_{Bur}$ (percent buried volume) of each complex using the *SambVca* web application (Table 2).[17] As already witnessed with other metals,the introduction of methyl groups on the NHC backbone (**2a** vs **2b** and **4a** vs **4b**), which push the aromatic moieties towards the metal center, induces an increase in $\%V_{Bur}$ in each case. The increase of the sterical hindrance also results in a longer NHC-metal distance. In comparison, ligand IPr* was found to be extremely hindered as $\%V_{Bur}$ calculated for **2e** reaches a value of 52.9 while the $\%V_{Bur}$ of the isopropyl analogues do not exceed the value of 42.8.

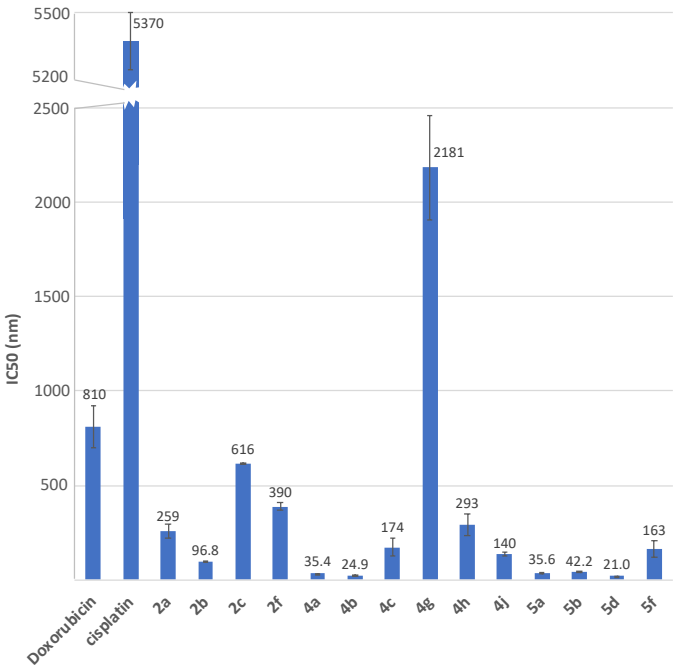
Since homoleptic silver(I) complexes featuring benzimidazole[6e] or imidazopyridine-based[6f] NHC ligand have already shown promising activity against colorectal HCT116 cancer cell lines compared to 5-fluorouracil or cisplatin, respectively, the unique capacity of mechanochemistry to generate rapidly a library of NHC silver complexes (**2a-5f)** prompted us to evaluate their cytotoxicity against this cell line.[16] The percentage inhibition of cell proliferation was firstly measured using 10^{-5} and 10^{-6} M solutions of the complexes (Figure 3). Half growth inhibition concentration (IC_{50}) was then measured only for compounds that showed high % of inhibition at 10^{-6} M (Figure 4). As a comparison, doxorubicin and cisplatin, which are commonly used to treat cancer, were evaluated on the same cancer cell line and possess IC_{50} of 810 nM and 5.37 µM, respectively. In addition, [AgClIPr] **2f** and $[Ag(IPr)_2]PF_6$ **4j** complexes were also tested to evaluate the influence of substitutions of the

Figure 3. Percentage of inhibition against HCT116 carcinoma cells at 10^{-5} and 10^{-6} M



ligand on cytotoxicity. Among the neutral heteroleptic complexes **2a-f**, only **2d** and **2e** were found almost inactive. Such behavior could be assigned to the poor solubility of the complexes in DMSO. Complex **2a** showed an IC_{50} of 259 nM. As a comparison, **2f**, which contains the classical IPr ligand, exhibited an IC_{50} of 390 nM, thus showing the positive influence of the methoxy groups on the NHC. The introduction of methyl group on the backbone of the NHC resulted in another positive effect as **2b** was found to be active at 96.8 nM. On the other hand, **2c**, featuring chlorine atoms on the backbone of the NHC, displayed an IC_{50} of 616 nM. Cationic homoleptic complexes having *N*,*N*-diaryl NHC ligands **4a-c** displayed a higher cytotoxicity, with IC_{50} values down to 24.9 nM for **4b**. Once again, the positive effect of the methoxy group

Figure 4. IC_{50} (nM) values against HCT116 carcinoma cells



was demonstrated as $[Ag(IPr)_2]PF_6$ complex displayed on IC_{50} of 140 nM (35.4 nM for **4a**). The addition of methyl goups on the NHC backbone results in even lower IC_{50} value (35.4 nM for **4a** vs 24.9 nM for **4b**). Homoleptic complexes **4f-i**, containing *N*-aryl, *N*-alkyl NHC ligands, were found to be less active. In this family, **4h** was the most active, with an IC_{50} at 293 nM. Cationic bis-NHC silver complexes **5a-f** also showed promising activity. **5a**, featuring an IMes ligand, was more cytotoxic than **5b** that contains the analogous saturated ligand. While very similar in structure, **5d**, having one IPr ligand in place of $^{Me}IPr^{OMe}$, was found to be slightly more active than homoleptic **4b**, with the best IC_{50} of 21 nM. **4b** is thus 256 and 38 times more active than cisplatin and doxorubicin, respectively. Interestingly, **5f**, containing a TPT ligand, showed an IC_{50} of 163 nM, thus demonstrating a possible diversification of the structure of the active complexes. On the other hand, **5c** and **5e**, featuring a ^{Cl}IPr and a *N*,*N*-dibenzyl NHC ligand, respectively, were not as active, with a % inhibition of cell proliferation below the values obtained for the other complexes. Thus, this preliminary study shows that introducing chlorine atoms on the backbone of the NHC, or using *N*-alkyl, *N*-aryl NHC ligands is detrimental to the biological activity. On the other hand, the $^{Me}IPr^{OMe}$ ligand, either in neutral heteroleptic or cationic complexes, seems to present the best positive effect on the cytotoxicity of the silver complexes. Of note, apart from **4g**, all the silver complexes tested displayed a higher cytotoxicity than doxorubicin and cisplatin.

In conclusion, Mechanochemistry overcame solution-based chemistry, permitting to access rapidly and efficiently novel families of neutral heteroleptic and cationic homo- and heteroleptic complexes featuring NHC ligands bearing sterically hindering groups, and also electron-donating or -withdrawing substituents. Importantly, the use of ball-mills enabled the isolation of complexes difficult if not impossible to prepare and isolate using solution-based strategy. As preliminary results, the silver complexes showed high cytotoxic activity against colorectal HCT116 cancer cell line, with IC_{50} down to 21 nM, which is 256 times better than cisplatin.

Acknowledgements

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Solving the Challenging Synthesis of Highly Cytotoxic Silver Complexes bearing Sterically Hindered NHC Ligands with Mechanochemistry

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Table of Content

I. General Information

All reagents were purchased from Sigma Aldrich, Fluka, Acros or Alfa Aesar. The milling treatments were carried out either in a vibrating Retsch Mixer Mill 200 or 400 (vbm) operated at up to 30 Hz, in a planetary ball-mill Retsch PM100 (pbm) operated at 450 rpm or in a planetary ball-mill Fritsch pulverisette 7 operated at 650 rpm or 800 rpm. Milling load (ML) is defined as the ratio between the mass of the reactants over the free volume of the jar. All of reaction mixtures were recovered with a solvent and filtrated over celite to remove metallic particles lost by the reactor during ball milling.

NMR Analyses were performed at the 'Laboratoire de Mesures Physiques' (IBMM, Université de Montpellier). ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 MHz, a Bruker AVANCE III 500 MHz or a Bruker AVANCE III 600 MHz and are reported in ppm using deuterated solvent ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm, acetone-d_6 at 2.05 ppm or $MeOD_4$ at 3.49 ppm) as internal standards. Data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet ; coupling constant in Hz; integration. ^{13}C-{^{1}H} NMR spectra were recorded on a Bruker AVANCE 101 MHz, a Bruker AVANCE III 126 MHz or a Bruker AVANCE III 151 MHz and are reported in ppm using deuterated deuterated solvent ($CDCl_3$ at 77.2 ppm or DMSO-d_6 at 39.5 ppm or acetone-d_6 at 29.8 ppm or MeOD-d_4 at 50.4 ppm) as internal standards.

Solid-State NMR spectra were recorded on a Varian VNMRS600 spectrometer (Larmor frequencies: ν^{1}H = 599.818 MHz and ν^{13}C = 150.839 MHz) using a 3.2 mm magic angle spinning (MAS) probe (T3 Wide Bore HX). Values of the isotropic chemical shifts of ^{1}H and ^{13}C are given using a secondary reference: Adamantane (1.8 ppm for ^{1}H and 38.5 ppm for ^{13}C). For the imidazolium salt, the studies were carried out with a $\pi/2$ pulse length of 4 µs, and a recycle delay of 10 s for 1H and 5 s for 13C. The used contact time is 2 ms. For the silver complex, the studies were carried out with a $\pi/2$ pulse length of 7 µs, and a recycle delay of 1 s for ^{1}H and 2 s for ^{13}C. The used contact time is 1 ms.

Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer and wavelength numbers of the relevant bands are reported in cm^{-1}.

Mass spectra were obtained by LC-MS with ESI using a Water Alliance 2695 as LC, coupled to a Waters ZQ spectrometer with electrospray source, a simple quadrupole analyzer and a UV Waters 2489 detector. HRMS analyses were performed on UPLC Acquity H-Class from Waters hyphenated to a Synapt G2-S mass spectrometer with a dual ESI source from Waters. High resolution MS analyses were performed on UPLC Acquity H-Class from Waters hyphenated to a Synapt G2-S mass spectrometer with a dual ESI source from Waters. ASAP analysis were performed on Synapt G2-S mass spectrometer from Waters, in a positive mode. HPLC conversion was measured on an Agilent technologies 1220 Infinity LC using a Chromolith® high resolution RP-18^{e} 50-4.6 mm column and a linear gradient of 0 to 100% CH_3CN/0.1% TFA in H_2O/0.1% TFA over 3 min (detection at 214 nm, flow rate: 1 ml/min).

Human HCT116 cancer cell line was obtained from the American type Culture Collection (ATCC, Rockville, MD) and was grown in Gibco McCoy's 5A supplemented with 10% fetal calf serum (FCS) and 1% glutamine according to the supplier's instructions. Cell line was

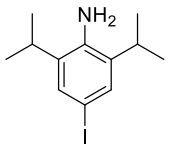
maintained at 37°C in a humidified atmosphere containing 5% CO_2. Cell viability was determined by a luminescent assay according to the manufacturer's instructions (Promega, Madison, WI, USA). For IC_{50} determination, the cells were seeded in 96-well plates (3×10^3 cells/well) containing 100 μL of growth medium. After 24 h of culture, the cells were treated with the tested compounds at 10 different final concentrations. Each concentration was obtained from serial dilutions in culture medium starting from the stock solution. Control cells were treated with the vehicle. Experiments were performed in triplicate. After 72 h of incubation, 100 μL of CellTiter Glo Reagent was added for 15 min before recording luminescence with a spectrophotometric plate reader PolarStar Omega (BMG LabTech). The dose-response curves were plotted with Graph Prism software and the IC_{50} values were calculated using the Graph Prism software from polynomial curves (four or five-parameter logistic equations).

II. General procedure for the synthesis of imidazolium salts

A. Synthesis of halogenated imidazolium salts

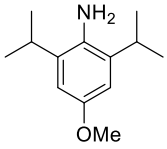
1. IPr^{OMe}.HCl **1a**

[1,3-Bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium chloride



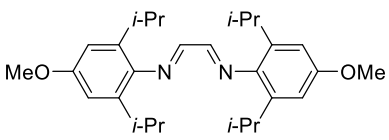
Following the reported procedure[1] and using 2,6-di*iso*propylaniline (17.1 mL, 90.7 mmol, 1.00 eq),.9 g, ICl solution 1M in DCM (100 mL, 100.0 mmol, 1.10 eq), sodium bicarbonate (22273 mmol, 3.00 eq) and MeOH (200 mL), the pure 4-iodo-2,6-di*iso*propylaniline was obtained (26.8 g, 88.4 mmol, 97%) as brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H), 2.85 (sept, *J* = 6.8 Hz, 2H), 1.24 (d, *J* = 6.8 Hz, 12H), NH_2 was not observed. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[2]



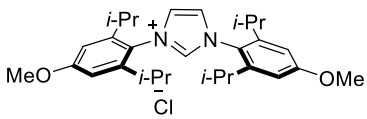
Following the reported procedure[1] and using 4-iodo-2,6-di*iso*propylaniline (294 mg, 0.97 mmol, 1.00 eq), CuI (9.2 mg, 0.05 mmol, 5 mol%), tetramethylphenanthroline (23 mg, 0.10 mmol, 10 mol%), CsOH (948 mg, 2.91 mmol, 3.00 eq) and degassed dry toluene (60 mL), the 4-methoxy-2,6-di*iso*propylaniline (198 mg, 0.96 mmol, 98%) was obtained as a brown oil. Purification by flash chromatography on silica gel could be used to purify if necessary, eluent pentane/EtOAc 99:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55 (s, 2H), 3.78 (s, 3H), 2.98 (sept, *J* = 6.8 Hz, 2H), 1.27 (d, *J* = 6.8 Hz, 12H), NH_2 not observed. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[1]



Following reported procedure[3] and using 4-methoxy-2,6-di*iso*propylaniline (2.0 g, 9.65 mmol, 2.00 eq), glyoxal 40% w/w in water (0.55 mL, 4.82 mmol, 1.00 eq) and MeOH (20 mL), the *N*,*N'*-bis[(4-methoxy-2,6-di*iso*propyl)phenyl]ethane-1,2-diimine was obtained as a yellow powder (1.39 g, 3.18 mmol, 66%).

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 6.74 (s, 4H), 3.84 (s, 6H), 2.98 (sept, *J* = 6.8 Hz, 4H), 1.20 (d, *J* = 6.8 Hz, 24H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[4]

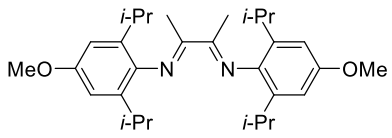


Using reported procedure by Nolan *et al.*[5] with *N*,*N'*-bis(4-methoxy-2,6-di*iso*propylphenyl)ethane-1,2-diimine (1.33 g, 3.05 mmol, 1.00 eq) in freshly distilled EtOAc (8 mL), paraformaldehyde (119.1 mg, 3.96 mmol, 1.30 eq) in a 4 M dioxane solution of HCl (1.22 mL, 4.88 mmol, 1.60 eq), pure [1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium chloride (956 mg, 1.97 mmol, 65%) were obtained as a white powder.

^{1}H NMR (400 MHz, MeOD-*d*$_4$) δ 9.89 (s, 1H), 8.19 (s, 2H), 7.00 (s, 4H), 3.92 (s, 6H), 2.45 (sept, *J* = 6.8 Hz, 4H), 1.33 (d, *J* = 6.8 Hz, 12H), 1.26 (d, *J* = 6.8 Hz, 12H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[3b, 6]

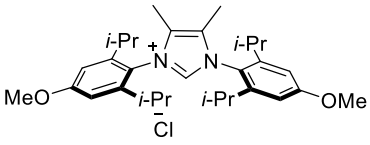
2. $^{Me}IPr^{OMe}$.HCl **1b**

[4,5-Dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium chloride



Following reported procedure[7] and using 4-methoxy-2,6-di*iso*propylaniline (386 mg, 1.86 mmol), 2,3-butanedione (66 µL, 0.75 mmol) and formic acid (99 drops) with methanol (12 mL), the pure *N*,*N*'-bis(4-methoxy-2,6-di*iso*propylphenyl)butane-2,3-diimine (196 mg, 0.42 mmol, 56%) was obtained as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 4H), 3.83 (s, 6H), 2.71 (sept, *J* = 6.8 Hz, 4H), 2.06 (s, 6H), 1.18 (d, *J* = 6.8 Hz, 12H), 1.16 (d, *J* = 6.8 Hz, 12H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[4]

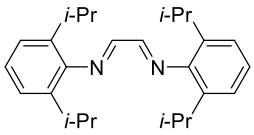


Using reported procedure by Nolan *et al.*[5] with *N*,*N*'-bis-(4-methoxy-2,6-di*iso*propylphenyl)butane-2,3-diimine (2.65 g, 5.70 mmol, 1.00 eq) in freshly distilled EtOAc (14 mL) and paraformaldehyde (222.6 mg, 7.41 mmol, 1.30 equiv.) in a 4 M dioxane solution of HCl (2.3 mL, 9.12 mmol, 1.60 eq), the pure [4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium chloride (1.68 g, 3.27 mmol, 58%) was obtained as a white powder

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 6.82 (s, 4H), 3.89 (s, 6H), 2.28 (sept, *J* = 6.7 Hz, 4H), 2.18 (s, 6H), 1.26 (d, *J* = 6.7 Hz, 12H), 1.25 (d, *J* = 6.7 Hz, 12H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[3b]

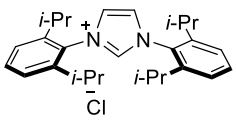
3. ^{Cl}IPr.HCl **1c**

[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium chloride



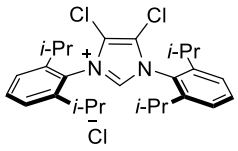
Following reported procedures[3] and using 2,6-di*iso*propylaniline (7.15 mL, 37.9 mmol, 2.20 eq), 40% glyoxal in water (2.0 mL, 17.2 mmol, 1.00 eq) and MeOH (40 mL), the *N*,*N*'-bis(2,6-di*iso*propylphenyl)ethane-1,2-diimine (5.12 g, 13.6 mmol, 79%) was obtained as a yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H) 7.11-7.23 (m, 6H), 2.94 (sept, *J* = 6.9 Hz, 4H), 1.21 (d, *J* = 6.9 Hz, 24H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[3a]



Using reported procedure by Nolan *et al.*[5] with *N*,*N*'-bis(2,6-di*iso*propylphenyl)ethane-1,2-diimine (30.0 g, 79.7 mmol, 1.00 eq) in freshly distilled EtOAc (32 mL) and paraformaldehyde (3.1 g, 103.6 mmol, 1.30 eq) in 4M hydrochloric acid in dioxane (31.9 mL, 127.5 mmol, 1.60 eq.), the pure 1,3-bis(2,6-di*iso*propylphenyl)imidazolium chloride (19.0 g, 44.7 mmol, 58%) was obtained as a white powder.

^{1}H NMR (400 MHz, MeOD-*d*$_4$) δ 9.98 (s, 1H), 8.29 (s, 2H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 4H), 2.50 (sept, *J* = 6.8 Hz, 4H), 1.35 (d, *J* = 6.8 Hz, 12H), 1.27 (d, *J* = 6.8 Hz, 12H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[3a]

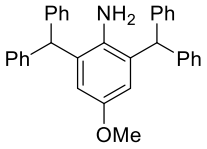


Using the reported procedure by Arduengo[3a] and using NaH (96 mg, 4.00 mmol, 2.00 eq), KO*t*Bu (a spatula) 1,3-bis(2,6-di*iso*propylphenyl)imidazolium chloride (850 mg, 2.00 mmol, 1.00 eq), CCl_4 (386 µL, 4.00 mmol, 2.00 eq) and dry and degassed THF (10 mL), the pure [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium chloride (661 mg, 1.34 mmol, 67%) was obtained as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.12 (s, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 4H), 2.33 (sept, *J* = 6.8 Hz, 4H), 1.36 (d, *J* = 6.8 Hz, 12H), 1.28 (d, *J* = 6.8 Hz, 12H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[3a]

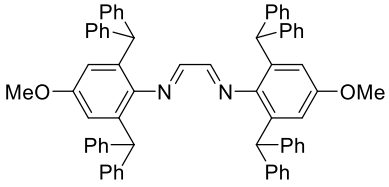
4. IPr*^{OMe}.HCl **1d**

[1,3-Bis(4-methoxy-2,6-diphenylmethyl)phenyl]imidazolium chloride



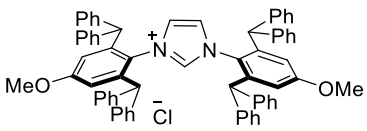
Following the reported procedure by Markó[8] and using diphenylmethanol (22.7 g, 123.2 mmol, 2.00 eq), 4-anisidine (7.39 g, 60.0 mmol, 1.00 eq) and a premade solution of HCl/$ZnCl_2$ (37% HCl in water, 5.6 mL, 60.0 mmol, 1.00 eq; $ZnCl_2$, 4.1 g, 30.0 mmol, 0.50 eq), the pure 4-methoxy-2,6-bis(diphenylmethyl)aniline (21.1 g, 46.3 mmol, 77%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.2 Hz, 8H), 7.21 (t, *J* = 8.2 Hz, 4H), 7.10 (d, *J* = 8.1 Hz, 8H), 6.19 (s, 2H), 5.48 (s, 2H), 3.42 (s, 3H), 3.17 – 3.08 (*br* s, 2H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[9]



Following reported procedure[7] and using glyoxal (0.22 mL, 1.92 mmol, 1.00 eq), 4-methoxy-2,6-bis(diphenylmethyl)aniline (1.75 g, 3.83 mmol, 2.00 eq), few drops of formic acid and MeOH (100 mL), the pure *N*,*N*'-bis(4-methoxy-2,6-(diphenylmethyl)phenyl)ethane-1,2-diimine (1.59 g, 1.70 mmol, 89%) was obtained as a yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (m, 26H), 7.24 (d, 16H), 6.42 (s, 4H), 5.26 (s, 4H), 3.51 (s, 6H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[9]

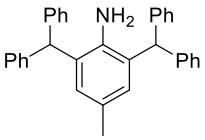


Following the procedure reported by Nolan *et al.*[5] and using *N*,*N*'-bis(4-methoxy-2,6-(diphenylmethyl)phenyl)ethane-1,2-diimine (8.0 g, 8.57 mmol, 1.00 eq) in THF (275 mL), and HCl/$ZnCl_2$/paraformaldehyde (HCl 4M in dioxane, 3.4 mL, 13.54 mmol, 1.50 eq; $ZnCl_2$, 1.17 g, 8.58 mmol, 1.00 eq; paraformaldehyde, 211.2 mg, 9.09 mmol, 1.05 eq), the pure [1,3-bis(4-methoxy-2,6-diphenylmethyl)phenyl]imidazolium chloride (2.1 g, 2.14 mmol, 25%) was obtained as an off white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.89 (s, 1H), 7.31-7.11 (m, 34H,), 7.15 (d, *J* = 7.1 Hz, 8H), 6.47 (s, 4H), 5.42 (s, 2H), 5.31 (s, 4H), 3.52 (s, 6H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[9]

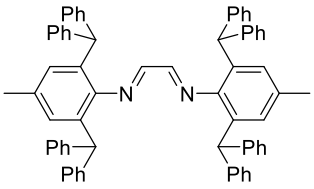
5. IPr*.HCl **1e**

[1,3-Bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazolium chloride



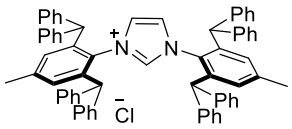
Following the reported procedure by Markó and co-worker[8] and using diphenylmethanol (22.7 g, 123.0 mmol, 2.00 eq) and 4-toluidine (6.43 g, 60.0 mmol, 1.00 eq) and a solution of HCl/$ZnCl_2$ (37% HCl in water, 5.6 mL, 60 mmol, 1.00 eq; $ZnCl_2$, 4.1 g, 30 mmol , 0.50 eq), the 4-methyl-2,6-diphenylmethylaniline (20.1 g, 45.7 mmol, 76%) was obtained as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 8H), 7.22 (t, *J* = 7.0 Hz, 8H), 7.10 (d, *J* = 6.8 Hz, 8H), 6.39 (s, 2H), 5.46 (s, 2H), 2.03 (s, 3H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[8]



Following the reported procedure by Markó and co-worker[8] and using 40% glyoxal in water (0.85 mL, 7.50 mmol, 1.00 eq), 4-methyl-2,6-diphenylmethylaniline (6.6 g, 15.0 mmol, 2.00 eq), formic acid (0.1 ml) and dichloromethane (150 mL), the pure *N*,*N*'-bis[(4-methyl-2,6-diphenylmethyl)phenyl]ethane-1,2-diimine (5.87 g, 6.51 mmol, 87%) was obtained as a yellow powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 6.6 Hz, 16H), 7.23-7.12 (m, 26H), 6.66 (s, 4H), 5.22 (s, 4H), 2.12 (s, 6H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[8]

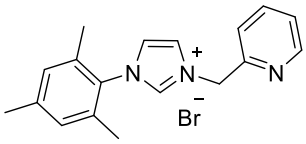


Following the procedure reported by Markó and co-worker[8] and using *N*,*N*'-bis[(4-methyl-2,6-diphenylmethyl)phenyl]ethane-1,2-diimine (2.5 g, 2.77 mmol, 1.00 eq) in $CHCl_3$ (30 mL), and a solution of HCl/$ZnCl_2$/paraformaldehyde (37% HCl in water, 0.60 mL, 6.72 mmol, 2.40 eq), $ZnCl_2$ (458 mg, 3.36 mmol, 1.20 eq) and paraformaldehyde (100.9 mg, 3.36 mmol, 1.20 eq), the pure [1,3-bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazolium chloride (1.35 g, 1.42 mmol, 51%) was obtained as an off white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.92 – 13.06 (*br* s, 1H), 7.28 – 7.08 (m, 24H), 6.88 – 6.65 (m, 12H), 5.46 (s, 2H), 5.29 (s, 4H), 2.18 (s, 6H). All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[8]

6. IMesPic.HBr **1f**

1-mesityl-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium bromide

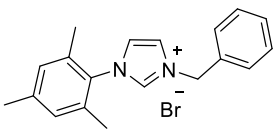


Bromomethylpyridine hydrobromide (120.0 mg, 0.48 mmol, 1.50 eq), sodium hydrogenocarbonate (59.9 mg, 0.71 mmol, 2.30 eq) and *N*-mesitylimidazole (59.47 mg, 0.32 mmol, 1.00 eq) were introduced in a 13 mL PTFE grinding bowl with one stainless steel ball (1 cm diameter). Total mass of the reagents has been calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding in the vibratory ball mill operated at 25 Hz for 1h30. Reaction mixture was recovered with water and ethyl acetate. The aqueous layer was washed 3 times with ethyl acetate, and evaporated to give a red powder. This powder was recovered with 2-propanol and filtrated over celite. The solvent was evaporated under vacuum to afford 1-mesityl-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium bromide (104.0 mg, 0.29 mmol, 91%) as a pale red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (t, *J* = 1.4 Hz, 1H), 8.78 (dd, *J* = 4.8, 1.6, 1H), 8.36 (t, *J* = 1.7 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 8.01 (td, *J* = 7.7, 1.8 Hz, 1H), 7.55 (dd, *J* = 7.6, 4.9, 1H), 7.47 (t, *J* = 1.8 Hz, 1H), 6.40 (s, 2H), 2.60 (s, 3H), 2.33 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.7, 149.7, 141.3, 138.1, 137.7, 134.3, 130.7, 129.8, 124.1, 124.0, 123.9, 122.7, 54.0, 21.1, 17.6. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[10]

7. IMesBn.HBr **1g**

1-Benzyl-3-mesitylimidazolium bromide

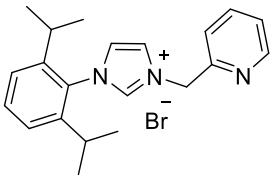


Benzyl bromide (77.8 µL, 0.65 mmol, 1.00 eq) and *N*-mesitylimidazole (128 mg, 0.69 mmol, 1.05 eq) were introduced in a 13 mL PTFE milling jar with one stainless steel ball (1 cm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding in the vibratory ball mill operated at 25 Hz for 1h. Reaction mixture was recovered with absolute ethanol and filtrated over celite. The solvent was evaporated under vacuum to afford 1-benzyl-3-mesitylimidazolium bromide (173.0 mg, 0.48 mmol, 97%) as a pale brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (t, *J* = 1.5 Hz, 1H), 7.80 (t, *J* = 1.7 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.33 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.14 (t, *J* = 1.8 Hz, 1H), 6.93 (s, 2H), 5.91 (s, 2H), 2.28 (s, 3H), 2.00 (s, 6H) ; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 141.3, 137.8, 134.2, 133.7, 130.7, 129.9, 129.43, 129.39, 129.2, 123.3, 123.1, 53.4, 21.1, 17.7. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[11]

8. IPrPic.HBr **1h**

1-(2,6-diisopropylphenyl)-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium

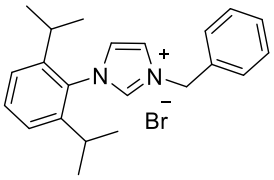


Bromomethylpyridine hydrobromide (113.9 mg, 0.45 mmol, 1.50 eq), sodium hydrogenocarbonate (56.7 mg, 0.68 mmol, 2.30 eq) and *N*-(2,6-diisopropyl)imidazole (68.9 mg, 0.30 mmol, 1.00 eq) were introduced in a 13 mL PTFE grinding bowl with one stainless steel ball (1 cm diameter). Total mass of the reagents has been calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding in the vibratory ball mill operated at 25 Hz for 1h45. Reaction mixture was recovered with water and ethyl acetate. The aqueous layer was washed, and evaporated to give a brown powder. This powder was recovered with 2-propanol and filtrated over celite. The solvent was evaporated under vacuum to afford 1-(2,6-diisopropylphenyl)-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium (109 mg, 0.27 mmol, 91%) as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.52 – 8.49 (m, 1H), 8.26 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.78 (td, *J* = 7.7, 1.7 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.32 (s, 1H), 7.30 (s, 1H), 7.12 (t, *J* = 1.6 Hz, 1H), 6.24 (s, 2H), 2.31 (dt, *J* = 13.6, 6.8 Hz, 2H), 1.22 (d, *J* = 6.8 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.8, 149.6, 145.6, 138.6, 138.0, 132.1, 124.9, 124.6, 124.2, 124.2, 123.4, 54.1, 28.8, 24.5, 24.3. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[10]

9. IPrBn.HBr **1i**

3-benzyl-1-(2,6-diisopropylphenyl)-1H-imidazol-3-ium bromide



Benzyl bromide (69.5 µL, 0.58 mmol, 1.00 eq) and *N*-(2,6-diisopropyl)imidazole (140.2 mg, 0.61 mmol, 1.05 eq) were introduced in a 13 mL PTFE grinding bowl with one stainless steel ball (1 cm diameter). Total mass of the reagents has been calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding in the vibratory ball mill operated at 25 Hz for 1h30. Reaction mixture was recovered with absolute ethanol and filtrated over celite. The solvent was evaporated under vacuum to afford 3-benzyl-1-(2,6-diisopropylphenyl)-1H-imidazol-3-ium bromide (214.8 mg, 54 mmol, 93%) as a pale brown solid.

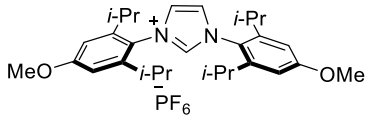
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 7.66 (s, 1H), 7.60 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.43 – 7.40 (m, 3H), 7.31 (s, 1H), 7.29 (s, 1H), 7.11 (s, 1H), 6.07 (s, 2H), 2.27 (dt, *J* = 13.6, 6.8 Hz, 2H), 1.23 (d, *J* = 6.8 Hz, 6H), 1.13 (d, *J* = 6.8 Hz, 6H) ; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.5, 138.7, 133.6, 132.1, 129.7, 129.3, 124.9, 124.1, 122.7, 54.0, 29.0, 24.6, 24.3. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[11]

B. Synthesis of hexafluorophosphate imidazolium salts

General procedure A: Imidazolium (1.00 eq) was dissolved in water and potassium hexafluorophosphate (1.20 eq) was added. The resulting suspension was stirred for 30 minutes and filtrated under vacuum. The solid was washed with water and diethyl ether and dried under vacuum to afford the product.

General procedure B : Imidazolium (1.00 eq) and potassium hexafluorophosphate (1.05 eq) were introduced in a 13 mL PTFE grinding bowl with one stainless steel ball (1 cm diameter). Total mass of the reagents has been calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding in the vibratory ball mill. Reaction mixture was recovered with dichloromethane, filtrated over celite and the solvent was evaporated under vacuum. The residue was then washed with water three times and diethyl ether twice. The product was dried under vacuum to afford hexafluorophosphate imidazolium salt.

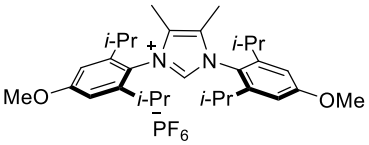
[1,3-Bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium hexafluorophosphate 3a



General procedure A was followed with [1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium chloride (300 mg, 0.618 mmol) and potassium hexafluorophosphate (136.6 mg, 0.742 mmol) to afford [1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium hexafluorophosphate (328.3 mg, 0.552 mmol, 89%) as a white solid.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.03 (t, *J* = 1.5 Hz, 1H), 8.43 (s, 1H), 8.43 (s, 1H), 7.00 (s, 4H), 3.87 (s, 6H), 2.31 (sept, *J* = 6.8 Hz, 4H), 1.25 (d, *J* = 6.8 Hz, 12H), 1.15 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.5, 146.6, 140.0, 126.5, 122.9, 109.9, 55.7, 28.9, 24.0, 23.0; **^{31}P NMR (202 MHz, DMSO-*d*$_6$)** δ -144.2 (sept, *J* = 711.3 Hz); **HRMS** calcd for $C_{29}H_{41}N_2O_2$ $[M - PF_6^-]^+$: 449.3168; found: 449.3167.

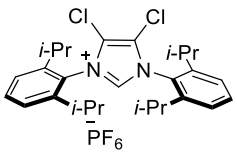
[4,5-Dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium hexafluorophosphate 3b



General procedure A was followed with [4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium chloride (300.0 mg, 0.585 mmol) and potassium hexafluorophosphate (129.1 mg, 0.702 mmol) to afford [4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium hexafluorophosphate (287.0 mg, 0.461 mmol, 79%) as a white solid.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 9.86 (s, 1H), 7.02 (s, 4H), 3.88 (s, 6H), 2.26 (sept, *J* = 6.8 Hz, 4H), 2.06 (s, 6H), 1.25 (d, *J* = 6.8 Hz, 12H), 1.11 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.6, 147.0, 137.4, 129.1, 120.6, 110.2, 55.7, 28.7, 24.6, 22.5, 8.4; **^{31}P NMR (202 MHz, DMSO-*d*$_6$)** δ -144.19 (sept, *J* = 711.2 Hz); **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -70.18 (d, *J* = 711.3 Hz); **HRMS** calcd for $C_{31}H_{45}N_2O_2$ $[M - PF_6^-]^+$: 477.3481; found: 477.3485.

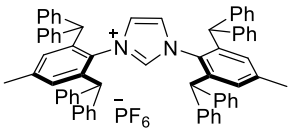
[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium hexafluorophosphate 3c



General procedure A was followed with [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium chloride (300.0 mg, 0.607 mmol) and potassium hexafluorophosphate (134.1 mg, 0.729 mmol) to afford [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium hexafluorophosphate (315.5 mg, 0.523 mmol, 86%) as a white solid.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.56 (s, 1H), 7.74 (t, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 4H), 2.53 – 2.47 (m, 4H) signal corresponding to the C**H**$(CH_3)_2$ under the residual signal of DMSO-*d*$_6$, 1.27 (d, *J* = 6.8 Hz, 12H), 1.13 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 145.8, 138.1, 133.1, 126.8, 125.3, 122.4, 28.5, 24.5, 22.8; **^{31}P NMR (202 MHz, DMSO-*d*$_6$)** δ -144.2 (sept, *J* = 711.2 Hz); **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -70.2 (d, *J* = 711.2 Hz); **HRMS** calcd for $C_{27}H_{35}N_2Cl_2$ $[M - PF_6^-]^+$: 457.2177; found: 457.2181.

[1,3-Bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazolium hexafluorophosphate 3d

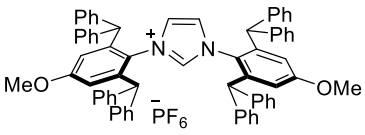


General procedure B was followed with [1,3-bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazolium chloride (350.0 mg, 0.369 mmol) and potassium hexafluorophosphate (81.5 mg, 0.369 mmol) to afford [1,3-bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazolium hexafluorophosphate (303.9 mg, 0.287 mmol, 78%) as a white solid.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.73 (s, 1H), 7.29 – 7.23 (m, 24H), 6.97 (s, 4H), 6.95 – 6.91 (m, 8H), 6.85 – 6.81 (m, 8H), 6.75 (d, *J* = 1.4 Hz, 2H), 4.89 (s, 4H), 2.23 (s, 6H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 141.7, 141.5, 141.3, 140.03, 139.99, 130.0, 129.6, 129.0, 128.85, 128.80, 128.7, 127.4, 127.2, 125.4, 51.0, 21.3; **^{31}P NMR (202 MHz, DMSO-*d*$_6$)** δ -144.2 (sept, *J* = 711.2 Hz); **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -70.2 (d, *J* = 711.2 Hz); **HRMS** calcd for $C_{69}H_{57}N_2$ $[M - PF_6^-]^+$: 913.4522; found: 913.4526.

^{1}H solid state NMR (600 MHz, none) δ 9.53, 9.05 – 4.83, 4.23, 3.55, 2.03, 1.21; **^{13}C solid state NMR (151 MHz, none)** δ 145.6, 144.3, 143.5, 142.8, 142.1, 139.7, 133.6, 131.9, 130.8, 129.9, 129.5, 129.2, 127.9, 126.5, 52.7, 52.2, 51.9, 22.2, 20.9.

[1,3-Bis(4-methoxy-2,6-diphenylmethyl)phenyl]imidazolium hexafluorophosphate 3e

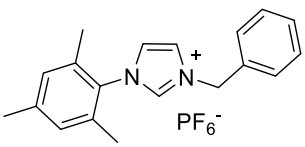


General procedure A was followed with [1,3-bis(4-methoxy-2,6-diphenylmethyl)phenyl]imidazolium chloride (400 mg, 0.422 mmol) and potassium hexafluorophosphate (93.1 mg, 0.506 mmol). 10 mL stainless steel jar was used and subjected to grinding in a vibratory ball mill operated at 30 Hz for 0.5 h to afford [1,3-bis(4-methoxy-2,6-diphenylmethyl)phenyl]imidazolium hexafluorophosphate (410 mg, 0.357 mmol, 92%) as a white solid.

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 10.56 (s, 1H), 7.29 – 7.22 (m, 24H), 6.94 – 6.90 (m, 8H), 6.83 – 6.79 (m, 8H), 6.54 (d, *J* = 1.4 Hz, 2H), 6.53 (s, 4H), 4.84 (s, 4H), 3.52 (s, 6H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)**

δ 160.9, 142.5, 141.6, 141.5, 140.9, 129.4, 129.3, 129.2, 129.1, 127.9, 127.8, 125.7, 125.1, 115.1, 55.8, 51.6; **HRMS** calcd for $C_{69}H_{57}N_2O_2$ $[M - PF_6^-]^+$: 945.4420; found: 945.4423.

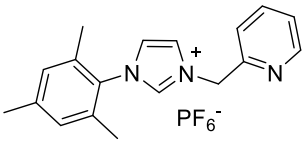
1-Benzyl-3-mesitylimidazolium hexafluorophosphate 3f



General procedure B was used with 1-benzyl-3-mesitylimidazolium bromide (155 mg, 0.44 mmol, 1.00 eq) and potassium hexafluorophosphate (84 mg, 0.46 mmol, 1.05 eq). The milling jar was subjected to grinding in the vibratory ball mill operated at 25 Hz for 0.5 h to afford 1-benzyl-3-mesitylimidazolium hexafluorophosphate (165 mg, 0.39 mmol, 89 %) as a pale brown solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.57 (s, 1H), 8.07 (s, 1H), 7.96 (t, *J* = 1.7 Hz, 1H), 7.45 (s, 5H), 7.16 (s, 2H), 5.53 (s, 2H), 2.34 (s, 3H), 2.01 (s, 6H) ; **^{13}C NMR (101 MHz, DMSO-d_6)** δ 140.3, 137.6, 134.7, 134.2, 131.1, 129.2, 128.8, 128.0, 124.3, 123.2, 52.4, 20.5, 16.8; **^{31}P NMR (162 MHz, DMSO- d_6)** δ -144.2 (hept, *J* = 710.6 Hz) ; **^{19}F NMR (376 MHz, DMSO- d_6)** δ -70.1 (d, *J* = 710.6 Hz).

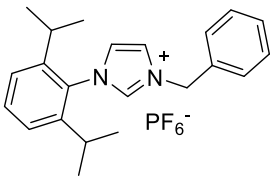
1-mesityl-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium hexafluorophosphate 3g



General procedure B was used with 1-mesityl-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium bromide (155 mg, 0.44 mmol, 1.00 eq) and potassium hexafluorophosphate (84 mg, 0.46 mmol, 1.05 eq). The milling jar was subjected to grinding in the vibratory ball mill operated at 25 Hz for 0.5 h to afford 1-mesityl-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium hexafluorophosphate (151 mg, 0.36 mmol, 81 %) as a pale brown solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.46 (s, 1H), 8.47 (d, *J* = 4.2 Hz, 1H), 7.96 (s, 1H), 7.88 – 7.81 (m, 2H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.08 (s, 2H), 5.60 (s, 2H), 2.26 (s, 3H), 1.97 (s, 6H) ; **^{13}C NMR (101 MHz, DMSO-d_6)** δ 153.3, 149.7, 140.4, 138.6, 137.6, 134.4, 131.2, 129.3, 124.0, 123.9, 123.8, 122.4, 53.3, 20.6, 16.9 ; **^{31}P NMR (162 MHz, DMSO- d_6)** δ -139.5 (hept, *J* = 711.3 Hz) ; **^{19}F NMR (376 MHz, DMSO- d_6)** δ -65.4 (d, *J* = 711.4 Hz).

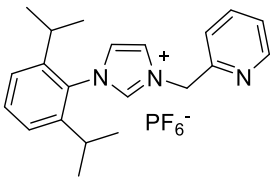
3-benzyl-1-(2,6-diisopropylphenyl)-1H-imidazol-3-ium hexafluorophosphate 3h



General procedure B was used with 3-benzyl-1-(2,6-diisopropylphenyl-1H-imidazol-3-ium bromide (161 mg, 0.41 mmol, 1.00 eq) and potassium hexafluorophosphate (78.3 mg, 0.43 mmol, 1.05 eq). The milling jar was subjected to grinding in the vibratory ball mill operated at 25 Hz for 0.5 h. to afford 3-benzyl-1-(2,6-diisopropylphenyl-1H-imidazol-3-ium hexafluorophosphate (182 mg, 0.39 mmol, 96 %) as a white solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 9.74 (s, 1H), 8.15 (dt, *J* = 8.4, 1.8 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.51 – 7.42 (m, 7H), 5.57 (s, 2H), 2.23 (dt, *J* = 13.6, 6.8 Hz, 2H), 1.14 (dd, *J* = 7.7, 7.1 Hz, 12H). ; **^{13}C NMR (125 MHz, DMSO-d_6)** δ 145.0, 140.2, 129.2, 129.1, 128.9, 128.7, 127.9, 127.9, 125.5, 125.4, 124.4, 124.4, 123.6, 52.6, 28.1, 23.8, 23.6 ; **^{31}P NMR (202 MHz, DMSO- d_6)** δ -144.2 (hept, *J* = 711.0 Hz) ; **^{19}F NMR (470 MHz, DMSO- d_6)** δ -70.2 (d, *J* = 711.0 Hz).

1-(2,6-diisopropylphenyl)-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium hexafluorophosphate 3i



General procedure B with 1-(2,6-diisopropylphenyl)-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium bromide (162 mg, 0.40 mmol, 1.00 eq) and potassium hexafluorophosphate (78.2 mg, 0.42 mmol, 1.05 eq). The milling jar was subjected to grinding in the vibratory ball mill operated at 25 Hz for 0.5 h. to afford 1-(2,6-diisopropylphenyl)-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium hexafluorophosphate (119 mg, 0.26 mmol, 64 %) as a pale red solid.

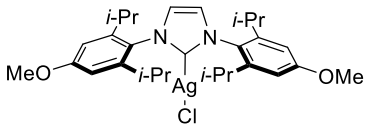
^{1}H NMR (500 MHz, DMSO-*d*$_6$) 9.65 (s, 1H), 8.51 (d, *J* = 4.8 Hz, 1H), 8.09 (dt, *J* = 10.7, 1.8 Hz, 2H), 7.92 (d, *J* = 1.8 Hz, 1H), 7.64 – 7.61 (t, J = 4.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.41 (dd, *J* = 7.1, 5.3 Hz, 1H), 5.70 (s, 2H), 2.38 – 2.35 (m, 1H), 1.17 – 1.12 (m, 12H) ; **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 153.2, 149.5, 145.2, 139.4, 137.6, 131.5, 130.7, 124.9, 124.4, 124.2, 123.7, 122.2, 53.2, 28.1, 23.9, 23.7 ; **^{31}P NMR (202 MHz, DMSO- *d*$_6$)** δ -144.2 (hept, *J* = 711.3 Hz) ; **^{19}F NMR (377 MHz, DMSO- *d*$_6$)** δ -70.2 (d, *J* = 711.3).

III. Synthesis of Silver(I)-carbene complexes in a ball-mill

A. Heteroleptic Silver(I)-carbene complexes mono-NHC

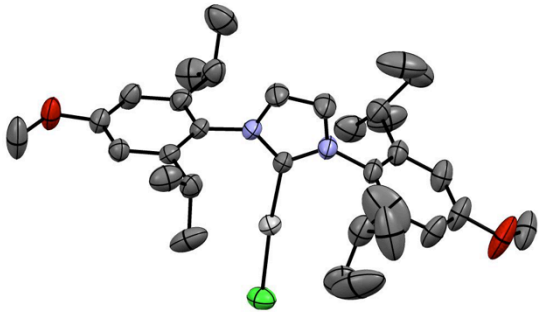
General procedure C : Imidazolium (1.00 eq) and silver oxide (0.55 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (1 cm diameter). Total mass of the reagents was calculated so that a milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding. The powder was recovered with dichloromethane, the suspension was filtrated over celite and the filtrate was concentrated under vacuum. The solid was washed with diethyl ether and dried to afford the product.

[[1,3-Bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazol-2-ylidene]silver chloride 2a



General procedure C was followed with [1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium chloride (144.1 mg, 0.297 mmol) and silver oxide (37.9 mg, 0.163 mmol). Reaction mixture was grinded for 3 hours at 30 Hz to afford [[1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazol-2-ylidene]silver chloride (143.3 mg, 0.242 mmol, 81%) as a white solid.

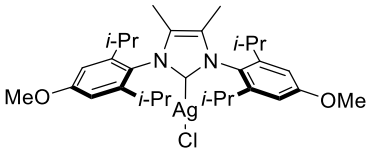
A mixture of [AgCl(IPr^{OMe})] and [AgCl(IPr^{OMe})$_2$] were obtained in 87:13 ratio. Followed, pics for the [AgCl(IPr^{OMe})] (major product) are reported: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.16 (s, 1H), 7.16 (s, 1H), 6.77 (s, 4H), 3.89 (s, 6H), 2.51 (sept, *J* = 6.9 Hz, 4H), 1.26 (d, *J* = 6.9 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 185.5 (dd, *J* = 256.3, 18.3 Hz), 161.0, 147.2, 127.8, 124.1, 124.0, 109.8, 55.5, 29.0, 24.8, 24.1. And followed, pics for the [AgCl(IPr^{OMe})$_2$] (minor product) are reported: **^{1}H NMR (500 MHz, $CDCl_3$)** 7.06 (d, *J* = 1.2 Hz, 4H), 6.60 (s, 8H), 3.95 (s, 12H), 2.24 (sept, *J* = 7.0 Hz, 8H), 1.07 (d, J = 7.0 Hz, 24H), 0.80 (d, *J* = 7.0 Hz, 24H); **^{13}C NMR (126 MHz, $CDCl_3$)** 184.1 (dd, *J* = 203.9, 14.4 Hz), 160.9, 146.8, 127.6, 125.21, 125.17, 109.6, 55.6, 28.8, 24.3, 24.1; **HRMS** calcd for $C_{29}H_{40}N_2O_2Ag$ $[M - Cl^-]^+$: 555.2141; found: 555.2145.



ORTEPs (at 50% probability level) of **2a**

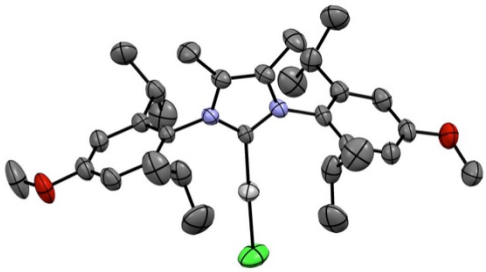
CCDC 1977192	**[AgCl(IPrOMe)] 2a**
Formula	$C_{29}H_{40}AgClN_2O_2$
M /g.mol^{-1}	591.95
Crystal system	monoclinic
Space group	P 2(1)/n
a/ Å	12.6677 (5)
b/ Å	12.5262 (6)
c/ Å	19.5459 (8)
α/ °	90
β/ °	103.521 (4)
γ/ °	90
V/ Å^3	3015.5 (2)
Z	4
ρ_{calcd}/g.cm^{-3}	1.304
μ (Mo Kα)/ mm^{-1}	0.783
T/ K	293 (2)
Number of reflections	46230
Number of unique reflections	7986
R_{int}	0.0403
*R*1, w*R*2 (I > 2σ(I))	0.0294, 0.0712
*R*1, w*R*2 (all data)	0.0434, 0.0765
GOF	1.033

[[4,5-Dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazol-2-ylidene]silver chloride 2b



General procedure C was followed with [4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium chloride (145.8 mg, 0.284 mmol) and silver oxide (36.2 mg, 0.156 mmol). Reaction mixture was grinded for 3 hours at 30 Hz to afford [[4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazol-2-ylidene]silver chloride (151.0 mg, 0.244 mmol, 86%) as a white solid.

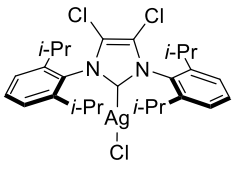
A mixture of [AgCl(MeIPr.OMe)] and [AgCl(MeIPr.OMe)$_2$] were obtained in 87:13 ratio. Followed, pics for the [AgCl(MeIPr.OMe)] (major product) are reported: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 6.78 (s, 4H), 3.89 (s, 6H), 2.40 (sept, *J* = 6.9 Hz, 4H), 1.93 (s, 6H), 1.25 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H) ; **^{13}C NMR (126 MHz, CDCl$_3$)** δ 181.3 (dd, *J* = 259.0, 18.6 Hz), 160.9, 147.5, 126.92, 126.87, 126.2, 109.9, 55.5, 28.9, 25.5, 23.4, 9.8 And followed, pics for the [AgCl(MeIPr.OMe)$_2$] (minor product) are reported: **^{1}H NMR (500 MHz, CDCl$_3$)** δ 6.61 (s, 8H), 3.97 (s, 12H), 2.16 – 2.11 (m, 8H), 1.75 (s, 12H), 1.06 (d, *J* = 6.9 Hz, 24H), 0.74 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR (126 MHz, CDCl$_3$)** δ 180.7 (dd, *J* = 204.8, 14.7 Hz), 160.7, 147.0, 127.73, 127.68, 126.2, 109.9, 55.5, 28.6, 25.3, 23.1, 9.9; **HRMS** calcd for $C_{31}H_{44}N_2O_2Ag$ [M – Cl$^-$]$^+$: 583.2454; found: 583.2460.



ORTEPs (at 50% probability level) of **2b**

CCDC 1977193	**[AgCl(^{Me}IPr^{OMe})] 2b**
Formula	$C_{31}H_{44}AgClN_2O_2$, $C_4H_{10}O$
M /g.mol^{-1}	694.12
Crystal system	monoclinic
Space group	P 2(1)/n
a/ Å	13.1039 (7)
b/ Å	21.2304 (10)
c/ Å	14.5112 (9)
α/ °	90
β/ °	112.345 (7)
γ/ °	90
V/ Å^3	3733.9 (4)
Z	4
ρ_{calcd}/g.cm^{-3}	1.235
μ (Mo Kα)/ mm^{-1}	0.644
T/ K	293 (2)
Number of reflections	51104
Number of unique reflections	9691
R_{int}	0.0666
*R*1, w*R*2 (I > 2σ(I))	0.0485, 0.1122
*R*1, w*R*2 (all data)	0.0752, 0.1224
GOF	1.039

[[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazol-2-ylidene]silver chloride 2c

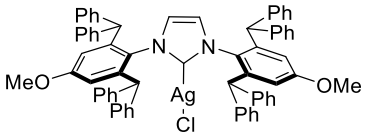


General procedure C was followed with [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium chloride (144.6 mg, 0.293 mmol) and silver oxide (37.3 mg, 0.161 mmol). Reaction mixture was grinded for 3 hours at 30 Hz to afford [[1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazol-2-ylidene]silver chloride (158.7 mg, 0.264 mmol, 90%) as a white solid.

A mixture of [AgCl(Cl.IPr)] and [AgCl(Cl.IPr)$_2$] were obtained in 95:5 ratio. Followed, pics for the [AgCl(Cl.IPr)] (major product) are reported: **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 4H), 2.46 (sept, *J* = 6.3 Hz, 4H), 1.28 (t, *J* = 6.3 Hz, 24H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ

183.9 (dd, *J* = 255.3, 18.3 Hz), 146.1, 131.85, 131.79i, 124.9, 119.8, 119.7, 29.2, 25.1, 23.5. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[12]

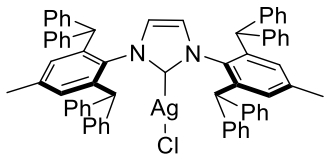
[[1,3-Bis(4-methoxy-2,6-diphenylmethyl)phenyl]imidazol-2-ylidene]silver chloride 2d



General procedure C was followed with [1,3-bis(4-methoxy-2,6-diphenylmethyl)phenyl]imidazolium chloride (161.0 mg, 0.164 mmol) and silver oxide (20.9 mg, 0.090 mmol). Reaction mixture was grinded for 3 hours at 30 Hz to afford [[1,3-bis(4-methoxy-2,6-diphenylmethyl)phenyl]imidazol-2-ylidene]silver chloride (159.5 mg, 0.146 mmol, 89%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 24H), 6.96 – 6.90 (m, 16H), 6.55 (s, 4H), 5.91 (s, 1H), 5.91 (s, 1H), 5.12 (s, 4H), 3.59 (s, 6H) ; **^{13}C NMR (126 MHz, $CDCl_3$)** δ 185.4 (dd, *J* = 251.3, 18.0 Hz), 160.2, 143.1, 142.8, 142.0, 129.9, 129.54, 129.47, 129.0, 128.6, 127.0, 123.94, 123.88, 115.2, 55.3, 51.5; **HRMS** calcd for $C_{69}H_{56}N_2O_2Ag$ $[M - Cl^-]^+$: 1051.3393; found: 1051.3392.

[[1,3-Bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazol-2-ylidene]silver chloride 2e



General procedure C was followed with [1,3-bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazolium chloride (160.4 mg, 0.169 mmol) and silver oxide (21.6 mg, 0.093 mmol). Reaction mixture was grinded for 3 hours at 30 Hz to afford [[1,3-bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazol-2-ylidene]silver chloride (144.4 mg, 0.137 mmol, 81%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.16 (m, 24H), 6.94 – 6.90 (m, 16H), 6.84 (s, 4H), 5.96 (s, 1H), 5.95 (s, 1H), 5.12 (s, 4H), 2.23 (s, 6H) ; **^{13}C NMR (126 MHz, $CDCl_3$)** δ 184.6 (dd, *J* = 251.5, 17.9 Hz), 143.3, 142.2, 140.9, 140.4, 134.5, 130.4, 129.6, 128.9, 128.6, 126.90, 126.86, 123.77, 123.71, 51.3, 21.9. All the resonances of ^{1}H and ^{13}C NMR spectra were consistent with reported values.[8]

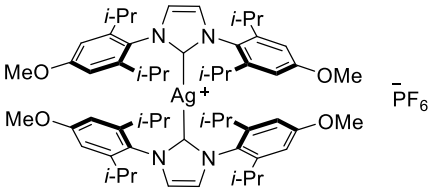
B. Homoleptic Silver (I)-carbene complexes

General procedure D: Imidazolium (1.00 eq), sodium hydroxide (1.10 eq) and silver oxide (0.50 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding in the vibratory ball mill operated at 30 Hz. The powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum. The solid was washed with diethyl ether and dried under vacuum to afford the product.

General procedure E: Hexafluorophosphate imidazolium salt (1.00 eq), silver oxide (0.75 eq) and sodium hydroxide (1.1 eq) were introduced in a 12 mL Stainless Steel grinding bowl with fifty stainless steel balls (0.5 cm diameter). Total mass of the reagents has been calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding in the planetary ball mill operated at 450 rpm for 5 h. Reaction mixture was recovered with dichloromethane, dried with

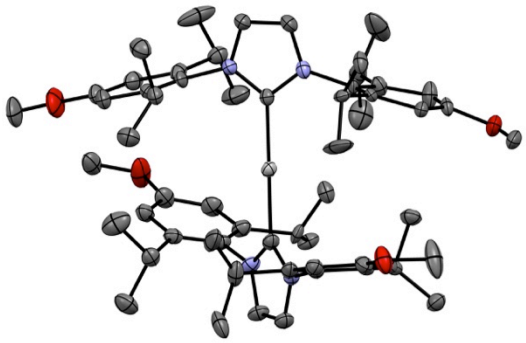
magnesium sulfate and filtrated over celite. The solvent was evaporated under vacuum to afford the desired homoleptic silver(I)-carbene complex.

Bis[(1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazol-2-ylidene]silver hexafluorophosphate 4a



General procedure D was followed with [1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium hexafluorophosphate (141.2 mg, 0.238 mmol), sodium hydroxide (10.4 mg, 0.261 mmol) and silver oxide (30.3 mg, 0.131 mmol). Reaction mixture was grinded for 3 hours to afford bis[(1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazol-2-ylidene]silver hexafluorophosphate (132.3 mg, 0.115 mmol, 97%) as a white solid.

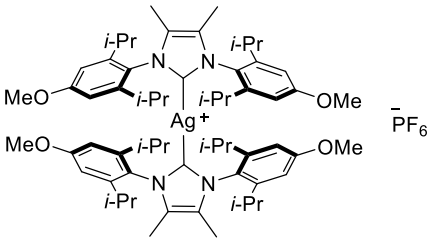
^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.68 (s, 2H), 7.68 (s, 2H), 6.65 (s, 8H), 3.90 (s, 12H), 2.18 (sept, *J* = 6.9 Hz, 8H), 1.01 (d, *J* = 6.8 Hz, 24H), 0.77 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 183.1 (dd, *J* = 201.3, 14.4 Hz), 160.6, 146.7, 128.0, 126.35, 126.31, 109.6, 55.8, 28.7, 24.1, 24.0; **^{31}P NMR (202 MHz, DMSO-*d*$_6$)** δ -144.2 (sept, *J* = 711.2 Hz); **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -70.2 (d, *J* = 711.2 Hz); **HRMS** calcd for $C_{58}H_{80}N_4O_4Ag$ $[M - PF_6^-]^+$: 1003.5231; found: 1003.5240.



ORTEPs (at 50% probability level) of **4a**

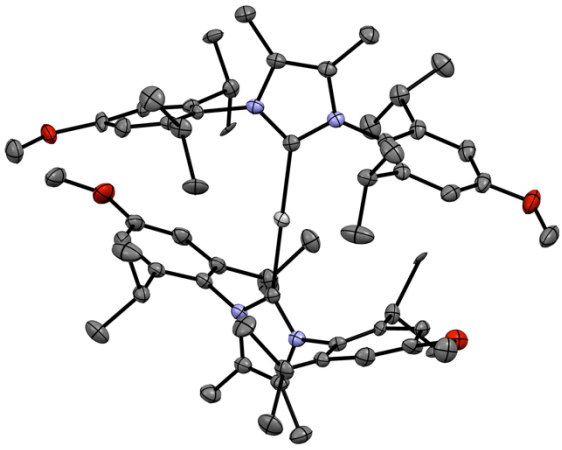
CCDC 1977190	**[Ag(IPrOMe)$_2$]PF$_6$ 4a**
Formula	$C_{58}H_{80}AgN_4O_4$, PF_6, $1/4CH_2Cl_2$
M /g.mol^{-1}	1192.56
Crystal system	Triclinic
Space group	P -1
a/ Å	12.5248 (4)
b/ Å	13.1434 (4)
c/ Å	20.5413 (6)
α/ °	82.614 (3)
β/ °	84.230 (2)
γ/ °	64.618 (3)
V/ Å^3	3025.82 (18)
Z	2
ρ_{calcd}/ g.cm^{-3}	1.309
μ (Mo Kα)/ mm^{-1}	0.469
T/ K	100 (2)
Number of reflections	39130
Number of unique reflections	13985
R_{int}	0.0608
*R*1, w*R*2 (I > 2σ(I))	0.0460, 0.1137
*R*1, w*R*2 (all data)	0.0672, 0.1222
GOF	1.057

Bis[(4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl)imidazol-2-ylidene]silver hexafluorophosphate 4b



General procedure D was followed with [4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium hexafluorophosphate (142.7 mg, 0.229 mmol), sodium hydroxide (10.1 mg, 0.252 mmol) and silver oxide (29.2 mg, 0.126 mmol). Reaction mixture was grinded for 3h to afford bis[(4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl)imidazole-2-ylidene]silver hexafluorophosphate (138.2 mg, 0.115 mmol, 100%) as a white solid.

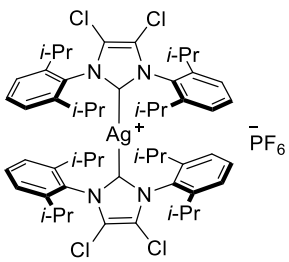
^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 6.66 (s, 8H), 3.93 (s, 12H), 2.11 (sept, *J* = 6.9 Hz, 8H), 1.71 (s, 12H), 1.01 (d, *J* = 6.9 Hz, 24H), 0.71 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 179.8 (dd, *J* = 204.2, 14.7 Hz), 160.1, 146.4, 127.4, 127.3, 125.7, 109.5, 55.3, 28.1, 24.7, 22.6, 9.3; **^{31}P NMR (202 MHz, DMSO-*d*$_6$)** δ -144.2 (sept, *J* = 711.2 Hz); **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -70.2 (d, *J* = 711.2 Hz); **HRMS** calcd for $C_{63}H_{84}N_8O_4Ag$ [M – PF_6^-]$^+$: 1059.5870; found: 1059.5861.



ORTEPs (at 50% probability level) of **4b**

CCDC 1977191	**[Ag(^{Me}IPr^{OMe})$_2$]PF$_6$ 4b**
Formula	$C_{62}H_{88}AgN_4O_4$, PF_6, CH_2Cl_2, 0.72 ($C_4H_{10}O$)
M /g.mol^{-1}	1291.12
Crystal system	orthorhombic
Space group	Ibca
a/ Å	20.9271 (5)
b/ Å	25.5794 (6)
c/ Å	25.7948 (6)
α/ °	90
β/ °	90
γ/ °	90
V/ Å^3	13808.0 (6)
Z	8
ρ_{calcd}/ g.cm^{-3}	1.242
μ (Mo Kα)/ mm^{-1}	0.453
T/ K	100
Number of reflections	140570
Number of unique reflections	9669
R_{int}	0.0580
*R*1, w*R*2 (I > 2*σ*(I))	0.0331, 0.0748
*R*1, w*R*2 (all data)	0.0482, 0.0806
GOF	1.054

Bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro)imidazol-2-ylidene]silver hexafluorophosphate 4c



General procedure D was followed with [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium hexafluorophosphate (141.7 mg, 0.235 mmol), sodium hydroxide (10.3 mg, 0.258 mmol) and silver oxide (29.9 mg, 0.129 mmol). Reaction mixture was grinded for 3 hours to afford bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro)imidazol-2-ylidene]silver hexafluorophosphate (116.1 mg, 0.0994 mmol, 85%) as a white solid.

Procedure in solution:

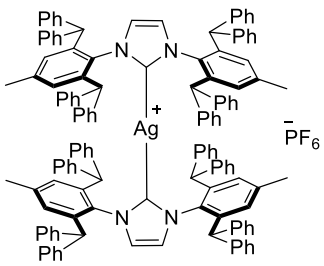
Protocol 1: In a solution of [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium hexafluorophosphate (50.0 mg, 82.9 µmol, 1.00 eq) in chloroform (830 µL), silver oxide (9.6 mg, 41.4 µmol, 0.50 eq) was added. The resulting suspension was stirred at reflux.

Protocol 2: In a solution of [1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium hexafluorophosphate (50.0 mg, 82.9 µmol, 1.00 eq) in dichloromethane (830 µL), silver oxide (9.6 mg, 41.4 µmol, 0.50 eq) and sodium hydroxide (3.4 mg, 91.2 µmol, 1.10 eq) was added. The resulting suspension was stirred at room temperature for 24h to afford bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro)imidazol-2-ylidene]silver hexafluorophosphate (21.9 mg, 18.8 µmol, 45%) as a white solid.

Entry	Procedure	Reaction time (h)	Conversion (%)	Yield (%)
1	Procedure in the ball-mill	3	100	85
2	Protocol 1	24	31	-
		48	90	-
3	Protocol 2	24	100	45

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.63 (t, *J* = 7.8 Hz, 4H), 7.28 (d, *J* = 7.8 Hz, 8H), 2.13 (sept, J = 6.9 Hz, 8H), 1.06 (d, *J* = 6.9 Hz, 24H), 0.73 (d, *J* = 6.9 Hz, 24H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 180.9 (dd, *J* = 212.4, 15.1 Hz), 145.0, 131.8, 130.9, 124.9, 120.4, 120.3, 28.3, 24.6, 22.7; **^{31}P NMR (202 MHz, DMSO-*d*$_6$)** δ -144.2 (sept, *J* = 711.2 Hz); **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -70.2 (d, *J* = 711.2 Hz); **HRMS** calcd for $C_{54}H_{68}N_4Cl_4Ag$ $[M - PF_6^-]^+$: 1019.3249; found: 1019.3256.

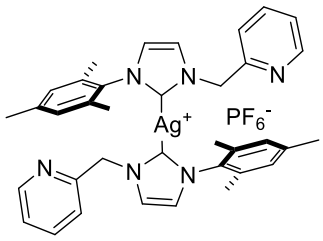
Bis[(1,3-bis(4-methyl-2,6-diphenylmethyl)phenyl)imidazol-2-ylidene]silver hexafluorophosphate 4e



General procedure D was followed with [1,3-bis(4-methyl-2,6-diphenylmethyl)phenyl]imidazolium hexafluorophosphate (158.1 mg, 0.149 mmol), sodium hydroxide (6.6 mg, 0.164 mmol) and silver oxide (17.3 mg, 0.075 mmol). Reaction mixture was grinded for 3h. Protocol 2 was followed to afford bis[(1,3-bis(4-methyl-2,6-diphenylmethyl)phenyl)imidazol-2-ylidene]silver hexafluorophosphate (139.4 mg, 0.069 mmol, 93%) as a white solid.

^{1}H solid state NMR (600 MHz, none) δ 8.95 – 4.12, 6.13, 2.99 – 0.55; **^{13}C solid state NMR (600 MHz, none)** 182.4, 149.5 – 138.0, 135.3, 133.7 – 120.5, 52.0, 22.0.

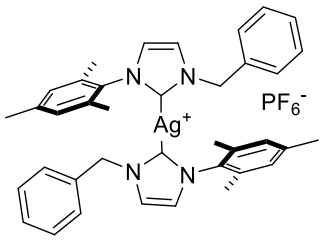
Bis[(1-(2-pyridyl)methylene-3-mesityl)imidazol-2-ylidene]silver hexafluorophosphate 4f



General procedure E was applied with 1-mesityl-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium (111 mg, 0.26 mmol, 1.00 eq), silver oxide (45.4 mg, 0.20 mmol, 0.75 eq) and sodium hydroxide (11.5 mg, 0.29 mmol, 1.1 eq) to afford Bis[(1-(2-pyridyl)methylene-3-mesityl)imidazol-2-ylidene]silver(I) hexafluorophosphate(V) (83.8 mg, 0.25 mmol, 80 %) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.49 (d, *J* = 4.3 Hz, 2H), 7.78 (td, *J* = 7.7, 1.7 Hz, 2H), 7.72 (t, *J* = 3.0 Hz, 2H), 7.45 (d, *J* = 1.6 Hz, 2H), 7.35 (dd, *J* = 6.8, 4.9 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.94 – 6.92 (m, 2H), 5.39 (s, 4H), 2.34 (s, 7H), 1.66 (s, 12H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 156.1, 149.4, 138.4, 137.2, 135.4, 134.2, 128.8, 123.1, 123.1 ; 121.3, 55.5, 20.6, 16.9. **^{31}P NMR (162 MHz, DMSO- d_6)** δ -144.3 (hept, *J* = 712.7 Hz) ; **^{19}F NMR (376 MHz, DMSO- d_6)** δ -73.1 (d, *J* = 712.7 Hz). **HRMS** calcd for $C_{36}H_{38}N_6Ag$ $[M - PF_6^-]^+$: 661.2203; found: 661.2312

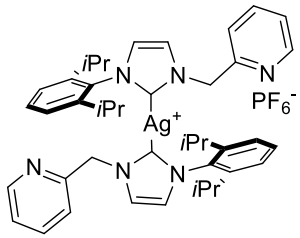
Bis[(1-benzyl-3-mesityl)imidazol-2-ylidene]silver hexafluorophosphate 4g



General procedure E was applied with 1-benzyl-3-mesitylimidazolium hexafluorophosphate (111 mg, 0.26 mmol, 1.00 eq), silver oxide (45.5 mg, 0.20 mmol, 0.75 eq) and sodium hydroxide (11.5 mg, 0.29 mmol, 1.1 eq) to afford Bis[(1-benzyl-3-mesityl)imidazol-2-ylidene)silver(I) hexafluorophosphate(V) (103 mg, 0.25 mmol, 97 %) as a white solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.70 (t, *J* = 1.5 Hz, 2H), 7.44 (t, *J* = 1.4 Hz, 2H), 7.32 (dd, *J* = 5.0, 1.8 Hz, 5H), 7.12 – 7.09 (m, 4H), 6.94 (s, 4H), 5.21 (s, 4H), 2.30 (s, 6H), 1.64 (s, 12H) ; **^{13}C NMR (126 MHz, DMSO-d_6)** 182.0 (d, *J* = 14.5 Hz), 180.5 (d, *J* = 14.5 Hz), 139.0, 137.7, 135.9, 134.7, 129.24 (d, *J* = 8.9 Hz), 128.5, 127.6, 123.9 (d, *J* = 6.4 Hz), 123.2 (d, *J* = 6.2 Hz), 54.29, 21.10, 17.39 ; **^{31}P NMR (162 MHz, DMSO-d_6)** δ -145.2 (hept, *J* = 712.7 Hz) **^{19}F NMR (377 MHz, DMSO-d_6)** δ -70.16 (d, J = 711.3 Hz). **HRMS** calcd for $C_{38}H_{40}N_4Ag$ $[M - PF_6^-]^+$: 659.2298; found: 659.2304.

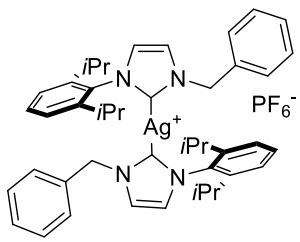
Bis[(1-(2-pyridyl)methylene-3-(2,6-diisopropylphenyl))imidazol-2-ylidene]silver hexafluorophosphate 4h



General procedure E was applied with 1-(2,6-diisopropylphenyl)-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium hexafluorophosphate (114 mg, 0.25 mmol, 1.00 eq), silver oxide (42.6 mg, 0.18 mmol, 0.75 eq) and sodium hydroxide (10.8 mg, 0.27 mmol, 1.1 eq) to afford **Bis[(1-(2-**pyridyl)methylene-3-(2,6-diisopropylphenyl))imidazol-2-ylidene]silver(I) hexafluorophosphate(V) (78 mg, 0.25 mmol, 70 %) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, 2H), 7.29 (dd, 6H), 7.21 (t, 2H), 7.13 (d, 4H), 6.99 – 6.96 (m, 6H), 5.05 (s, 4H), 2.24 (sept, 4H), 1.06 (d, 12H), 0.89 (d, 12H) ; **^{13}C NMR (126 MHz, $CDCl_3$)** δ 183.5, 154.9, 149.5, 145.8, 137.4, 134.7, 130.3, 123.9, 123.3, 122.4, 122.4, 122.2, 56.4, 28.1, 24.6, 23.9 ; **^{31}P NMR (162 MHz, $CDCl_3$)** δ -144.4 (hept, *J* = 712.9 Hz) ; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -73.4 (d, *J* = 712.9 Hz). **HRMS** calcd for $C_{42}H_{50}N_6Ag$ $[M - PF_6^-]^+$: 745.3148; found: 745.3262.

Bis[(1-benzyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene]silver hexafluorophosphate 4i



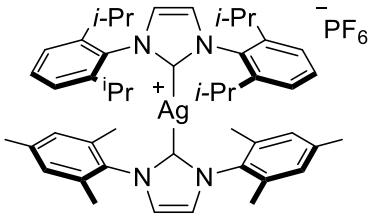
General procedure E was applied with 3-benzyl-1-(2,6-diisopropylphenyl)-1H-imidazol-3-ium hexafluorophosphate (114 mg, 0.25 mmol, 1.00 eq), silver oxide (42.7 mg, 0.18 mmol, 0.75 eq) and sodium hydroxide (10.8 mg, 0.29 mmol, 1.1 eq) to afford Bis[(1-benzyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene]silver(I) hexafluorophosphate(V) (98 mg, 0.25 mmol, 88 %) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.8 Hz, 2H), 7.29 (dd, *J* = 4.9, 1.7 Hz, 6H), 7.21 (t, *J* = 1.6 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 4H), 6.99 – 6.96 (m, 6H), 5.05 (s, 4H), 2.24 (dt, *J* = 13.8, 6.9 Hz, 4H), 1.06 (d, *J* = 6.9 Hz, 12H), 0.89 (d, *J* = 6.9 Hz, 12H) **^{13}C NMR (151 MHz, $CDCl_3$)** δ 182.0 (dd, *J* = 197.5, 14.5), 146.0, 136.0, 134.7, 130.6, 12.4, 129.1, 129.0, 128.5, 127.8, 127.0, 124.5, 124.5, 124.2, 122.9, 122.4, 122.4 ; **^{31}P NMR (162 MHz, $CDCl_3$)** δ -144.4 (hept, *J* = 712.6 Hz) ; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -73.4 (d, *J* = 712.6 Hz). **HRMS** calcd for $C_{44}H_{52}N_4Ag$ [M – PF_6^-]$^+$: 743.3243; found: 743.3248.

C. Heteroleptic silver-carbene complexes bis-NHC

General procedure F: [AgCl(IPr)] (1.00 eq), sodium hydroxide (1.10 eq) and corresponding imidazolium hexafluorophosphate (1.00 eq) were introduced in a 10 mL stainless steel grinding bowl with one stainless steel ball (10 mm diameter). Total mass of the reagents was calculated so that milling load equals 19.2 mg/mL. The bowl was closed and subjected to grinding in the vibratory ball mill operated at 30 Hz for 1 h. The powder was recovered with dichloromethane and the suspension was filtrated over celite. The filtrate was concentrated under vacuum. The solid was washed with diethyl ether and dried under vacuum to afford the pure product.

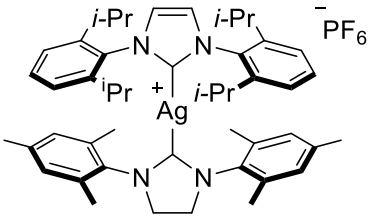
[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3-Bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene]silver hexafluorophosphate 5a



General procedure F was followed with [AgCl(IPr)] (94.3 mg, 0.18 mmol, 1.00 eq), sodium hydroxide (7.8 mg, 0.20 mmol, 1.10 eq) and [1,3-Bis(2,4,6-trimethylphenyl)]imidazolium hexafluorophosphate (79.9 mg, 0.18 mmol, 1.00 eq) to afford [[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3-Bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene]silver hexafluorophosphate (151.5 mg, 0.16 mmol, 90 %) as a solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.54 (t, *J* = 7.7 Hz, 2H), 7.19 (m, 4H), 6.99 (s, 2H), 6.81 (s, 4H), 2.39 (s, 6H), 2.25 (dt, *J* = 13.5, 6.9 Hz, 4H), 1.68 (s, 12H), 1.12 (d, *J* = 6.8 Hz, 12H), 0.81 (d, *J* = 6.8 Hz, 12H); **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 185.3 (d, $J_{H\text{-}Ag109}$ = Hz), 183.7 (d, $J_{H\text{-}Ag107}$ = Hz), 182.4 (d, $J_{H\text{-}Ag109}$ = Hz), 180.9 (d, $J_{H\text{-}Ag107}$ = Hz), 145.8, 139.7, 135.1, 134.7, 134.6, 131.0, 130.1, 124.4, 124.3, 123.8, 28.9, 24.7, 23.9, 21.4, 17.4; **^{31}P NMR (202 MHz, CD_2Cl_2)** δ -144.6 (sept, *J* = 710.4 Hz); **^{19}F NMR (376 MHz, CD_2Cl_2)** δ -73.7 (d, *J* = 710.3 Hz); **HRMS** calcd for $C_{48}H_{62}N_4Ag$ [M – PF_6^-]$^+$: 799.4020 ; found : 799.3887.

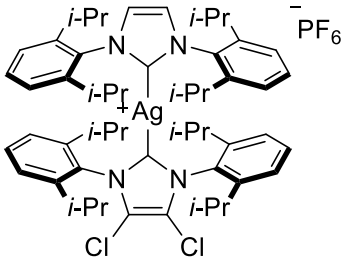
[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]silver hexafluorophosphate 5b



General procedure F was followed with [AgCl(IPr)] (94.1 mg, 0.18 mmol, 1.00 eq), sodium hydroxide (7.8 mg, 0.20 mmol, 1.10 eq) and [1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydro]imidazolium hexafluorophosphate (80.1 mg, 0.18 mmol, 1.00 eq) to afford [[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]silver hexafluorophosphate (153.2 mg, 0.16 mmol, 91 %) as a solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.55 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 4H), 7.15 (d, *J* = 1.0 Hz, 2H), 6.75 (s, 4H), 3.77 (s, 4H), 2.34 (s, 6H), 2.23 (sept, *J* = 6.9 Hz, 4H), 1.90 (s, 12H), 1.11 (d, *J* = 6.9 Hz, 12H), 0.81 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 205.985 (d, $J_{H\text{-}Ag109}$ = 200.0 Hz), 205.9735 (d, $J_{H\text{-}Ag107}$ = 172.8 Hz), 184.37 (d, $J_{H\text{-}Ag109}$ = 211.6 Hz), 184.37 (d, $J_{H\text{-}Ag107}$ = 183.7 Hz), 145.6, 138.7, 135.4, 134.9, 134.5, 131.0, 130.4, 124.4, 124.3, 124.2, 51.8, 51.7, 28.8, 24.5, 23.8, 21.3, 17.6; **^{31}P NMR (202 MHz, CD_2Cl_2)** δ -144.5 (sept, *J* = 710.3 Hz); **^{19}F NMR (376 MHz, CD_2Cl_2)** δ -73.6 (d, *J* = 710.3 Hz); **HRMS** calcd for $C_{48}H_{62}N_4Ag$ $[M - PF_6^-]^+$: 801.4025 ; found : 801.4019.

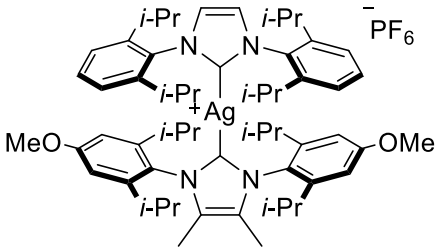
[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3-Bis(2,6-di*iso*propyl)phenyl]-4,5-dichloroimidazol-2-ylidene]silver hexafluorophosphate 5c



General procedure F was followed with [AgCl(IPr)] (82.1 mg, 0.15 mmol, 1.00 eq), sodium hydroxide (6.8 mg, 0.17 mmol, 1.10 eq) and 1,3-Bis(2,6-di*iso*propyl)phenyl]-4,5-dichloroimidazolium hexafluorophosphate (93.1 mg, 0.15 mmol, 1.00 eq) to afford [[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3-Bis(2,6-di*iso*propyl)phenyl]-4,5-dichloroimidazol-2-ylidene]silver hexafluorophosphate (148.7 mg, 0.14 mmol, 88 %) as a solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.56 (t, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 4H), 7.16 (d, *J* = 7.8 Hz, 4H), 7.07 (s, 1H), 7.07 (s, 1H), 2.26 (sept, J = 6.8 Hz, 4H), 2.15 (sept, *J* = 6.8 Hz, 4H), 1.11 (d, *J* = 6.8 Hz, 12H), 1.04 (d, *J* = 6.8 Hz, 12H), 0.79 (d, *J* = 7.0 Hz, 12H), 0.77 (d, *J* = 7.0 Hz, 12H); **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 182.248 (d, $J_{H\text{-}Ag109}$ = 219.7 Hz), 182.243 (d, $J_{H\text{-}Ag107}$ = 189.2 Hz), 181.913 (d, $J_{H\text{-}Ag109}$ = 226.4 Hz), 181.913 (d, $J_{H\text{-}Ag107}$ = 197.5 Hz), 146.2, 145.6, 134.9, 132.2, 131.8, 131.2, 125.44, 125.39, 125.2, 124.9, 121.0, 120.9, 29.2, 29.0, 25.4, 24.7, 24.2, 23.1; **^{31}P NMR (202 MHz, CD_2Cl_2)** δ -144.5 (sept, *J* = 710.2 Hz); **^{19}F NMR (376 MHz, CD_2Cl_2)** δ -73.6 (d, *J* = 710.2 Hz); **HRMS** calcd for $C_{54}H_{70}N_4Cl_2Ag$ $[M - PF_6^-]^+$: 951.4028; found : 951.4016.

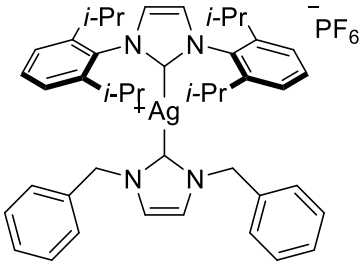
[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][(4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl)imidazol-2-ylidene]silver hexafluorophosphate 5d



General procedure F was followed with [AgCl(IPr)] (34.5 mg, 0.06 mmol, 1.00 eq), sodium hydroxide (2.9 mg, 0.07 mmol, 1.10 eq) and (4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl)imidazolium hexafluorophosphate (40.4 mg, 0.06 mmol, 1.00 eq) with a milling load equal to 8.3 mg/mL to afford [[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][(4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl)imidazol-2-ylidene]silver hexafluorophosphate (64.3 mg, 0.06 mmol, 89 %) as a solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.57 – 7.52 (m, 2H), 7.21 (dd, *J* = 7.5, 3.7 Hz, 4H), 7.10 (s, 1H), 7.10 (s, 1H), 6.66 (d, *J* = 3.4 Hz, 4H), 3.97 (s, 3H), 3.97 (s, 3H), 2.38 – 2.30 (m, 4H), 2.21 – 2.12 (m, 4H), 1.76 (d, *J* = 3.4 Hz, 6H), 1.11 (d, *J* = 6.9 Hz, 12H), 1.09 (d, *J* = 6.9 Hz, 12H), 0.89 (d, *J* = 3.5 Hz, 6H), 0.87 (d, *J* = 4.0 Hz, 6H), 0.77 (d, *J* = 3.5 Hz, 6H), 0.76 (d, *J* = 4.0 Hz, 6H); **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 183.56 (d, *J* = 213.1 Hz), 183.565 (d, *J* = 185.0 Hz), 180.045 (d, *J* = 222.3 Hz), 180.05 (d, *J* = 193.1 Hz), 161.0, 147.4, 145.7, 135.2, 131.1, 128.05, 128.01, 126.3, 125.31, 125.27, 124.7, 110.1, 55.7, 28.9, 25.8, 24.4, 24.2, 22.9, 9.8; **^{31}P NMR (202 MHz, CD_2Cl_2)** δ -144.5 (sept, *J* = 710.4 Hz); **^{19}F NMR (376 MHz, CD_2Cl_2)** δ -73.57 (d, *J* = 710.4 Hz); **HRMS** calcd for $C_{58}H_{80}N_4Ag$ $[M - PF_6^-]^+$: 743.3243; found : 743.3248.

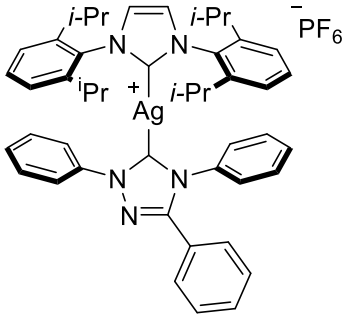
[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][*N,N*-dibenzylimidazolium]silver hexafluorophosphate 5e



General procedure E was followed with [AgCl(IPr)] (99.8 mg, 0.19 mmol, 1.00 eq), sodium hydroxide (8.3 mg, 0.21 mmol, 1.10 eq) and *N,N*-dibenzylimidazolium hexafluorophosphate (73.9 mg, 0.19 mmol, 1.00 eq) to afford [[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][*N,N*-dibenzylimidazolium]silver hexafluorophosphate (164.1 mg, 0.18 mmol, 99 %) as a solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.46 – 7.41 (m, 4H), 7.37 – 7.29 (m, 10H), 6.93 (s, 1H), 6.92 (s, 1H), 6.82 (d, *J* = 7.2 Hz, 4H), 4.69 (s, 4H), 2.57 (sept, *J* = 6.9 Hz, 4H), 1.27 (d, *J* = 6.9 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 184.68 (d, $J_{H\text{-}Ag109}$ = 211.6 Hz), 184.685 (d, $J_{H\text{-}Ag107}$ = 183.0 Hz), 179.65 (d, $J_{H\text{-}Ag109}$ = 212.2 Hz), 179.65 (d, $J_{H\text{-}Ag107}$ = 183.5 Hz), 146.2, 135.5, 134.7, 131.3, 129.4, 128.9, 127.4, 124.7, 124.64, 124.59, 122.6, 122.5, 55.5, 29.1, 25.0, 24.0; **^{31}P NMR (202 MHz, CD_2Cl_2)** δ -144.5 (sept, *J* = 710.4 Hz); **^{19}F NMR (376 MHz, CD_2Cl_2)** δ -73.4 (d, *J* = 710.4 Hz) ; **HRMS** calcd for $C_{44}H_{52}N_4Ag$ $[M - PF_6^-]^+$: 743.3243; found : 743.3248.

[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3,4-triphenyl-1,2,4-triazolium]silver hexafluorophosphate 5f



General procedure E was followed with [Ag(IPr)Cl] (102.6mg, 0.19 mmol, 1.00 eq), sodium hydroxide (8.5 mg, 0.21 mmol, 1.10 eq) and 1,3,4-triphenyl-1,2,4-triazolium hexafluorophosphate (70.8 mg, 0.21 mmol, 1.00 eq) to afford [[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3,4-triphenyl-1,2,4-triazolium]silver hexafluorophosphate (172.9 mg, 0.18 mmol, 95 %) as a solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.58 (t, *J* = 7.8 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.44 – 7.41 (m, 1H), 7.41 – 7.38 (m, 2H), 7.31 – 7.19 (m, 14H), 6.98 (dd, *J* = 8.4, 1.0 Hz, 2H), 2.39 (sept, *J* = 6.8 Hz, 4H), 1.17 (d, *J* = 6.9 Hz, 12H), 0.96 (d, *J* = 6.9 Hz, 12H) ; **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 182.835 (d, $J_{H\text{-}Ag109}$ = 225.9), 182.88 (d, $J_{H\text{-}Ag107}$ = 195.5), 182.05 (d, $J_{H\text{-}Ag109}$ = 207.1), 182.05 (d, $J_{H\text{-}Ag107}$ = 179.0), 154.64, 154.59, 145.89, 139.1, 135.9, 134.5, 131.7, 131.5, 131.0, 130.8, 130.4, 130.0, 129.24, 129.21, 126.5, 124.95, 124.90, 124.78, 124.1, 123.4, 28.9, 25.1, 23.7; **^{31}P NMR (202 MHz, CD_2Cl_2)** δ -144.5 (sept, *J* = 710.1 Hz). **^{19}F NMR (376 MHz, CD_2Cl_2)** δ -73.7 (d, *J* = 710.1 Hz) ; **HRMS** calcd for $C_{47}H_{51}N_5Ag$ $[M - PF_6^-]^+$: 792.3195; found : 792.3193.

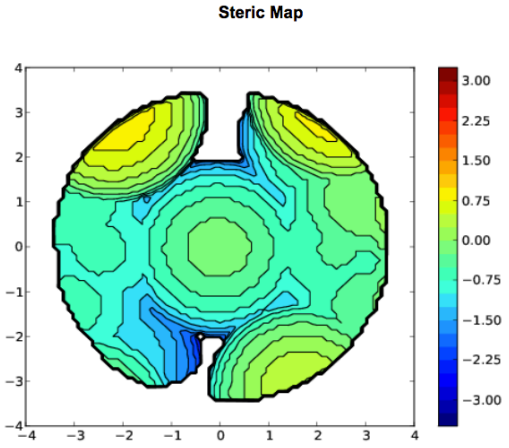
IV. %V_{Bur} calculations

A. %VBur for **2a** with real C-Ag distance, sphere radius of 3.5 Å.

V Free	V Buried	V Total	V Exact
107.4	72.1	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
59.8	**40.2**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	30.9	14.0	44.9	68.9	**31.1**
NW	25.2	19.7	44.9	56.2	**43.8**
NE	25.8	19.0	44.8	57.6	**42.4**
SE	25.4	19.4	44.9	56.6	**43.4**

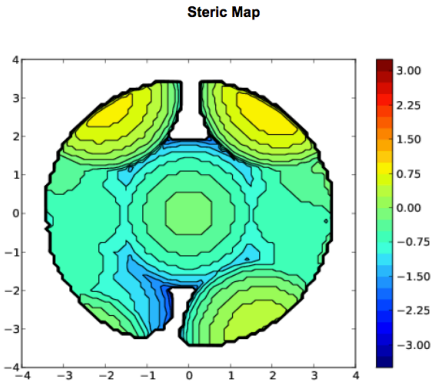


B. %VBur for **2a** with distance C-Ag normalized at 2.1 Å, sphere radius 3.5 Å.

V Free	V Buried	V Total	V Exact
105.3	74.2	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
58.7	**41.3**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	30.0	14.8	44.9	66.9	**33.1**
NW	25.0	19.9	44.9	55.7	**44.3**
NE	24.4	20.4	44.8	54.4	**45.6**
SE	25.9	19.0	44.9	57.6	**42.4**

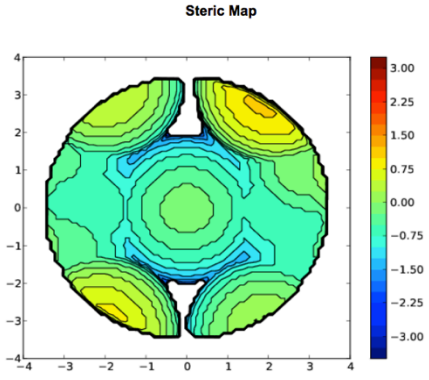


C. %VBur for **2b** with real C-Ag distance, sphere radius of 3.5 Å.

V Free	V Buried	V Total	V Exact
102.7	76.8	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
57.2	**42.8**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	25.2	19.7	44.9	56.1	**43.9**
NW	26.6	18.2	44.9	59.4	**40.6**
NE	23.4	21.4	44.8	52.2	**47.8**
SE	27.4	17.4	44.9	61.1	**38.9**

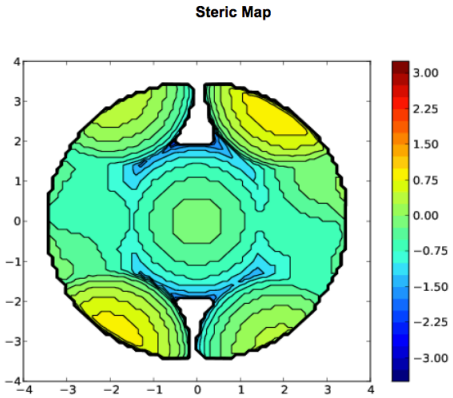


D. %VBur for **2b** with distance C-Ag normalized at 2.1 Å, sphere radius 3.5 Å.

V Free	V Buried	V Total	V Exact
103.2	76.3	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
57.5	**42.5**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	24.7	20.2	44.9	55.0	**45.0**
NW	27.2	17.7	44.9	60.6	**39.4**
NE	24.2	20.7	44.8	53.9	**46.1**
SE	27.1	17.7	44.9	60.5	**39.5**

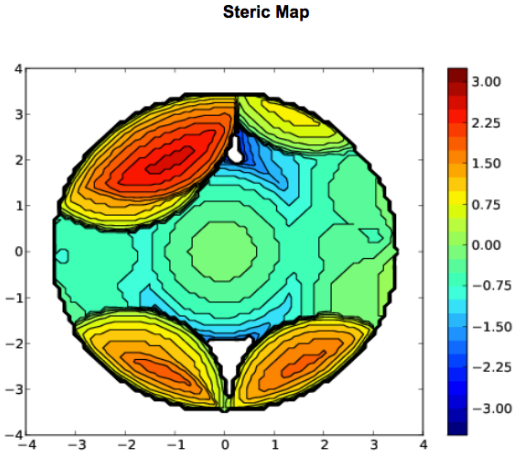


E. %VBur for **2e** with real C-Ag distance, sphere radius of 3.5 Å.

V Free	V Buried	V Total	V Exact
84.6	95.0	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
47.1	**52.9**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	21.8	23.1	44.9	48.5	**51.5**
NW	14.4	30.5	44.9	32.1	**67.9**
NE	26.4	18.4	44.8	58.9	**41.1**
SE	21.9	22.9	44.9	48.9	**51.1**

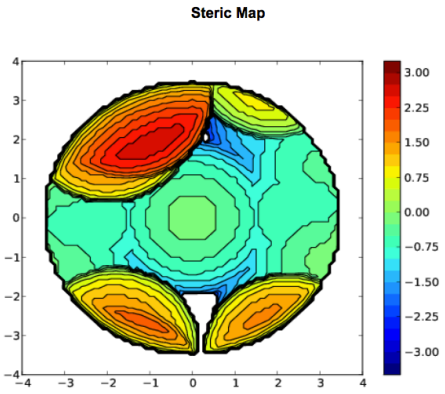


F. %VBur for **4a** with distance C-Ag normalized at 2.1 Å, sphere radius 3.5 Å.

V Free	V Buried	V Total	V Exact
84.6	94.9	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
47.1	**52.9**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	21.3	23.6	44.9	47.5	**52.5**
NW	12.5	32.3	44.9	27.9	**72.1**
NE	26.9	18.0	44.8	60.0	**40.0**
SE	23.8	21.0	44.9	53.2	**46.8**

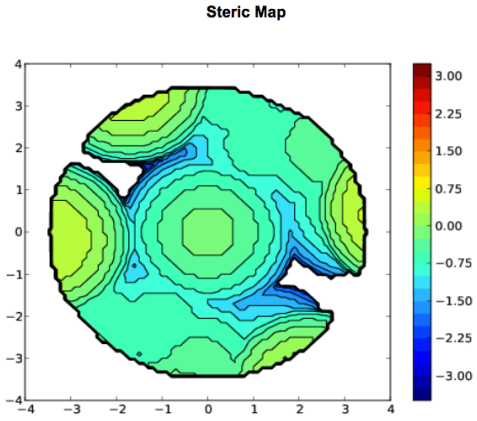


G. %VBur for **4a** with real C-Ag distance, sphere radius of 3.5 Å.

V Free	V Buried	V Total	V Exact
110.1	69.5	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
61.3	**38.7**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	26.1	18.8	44.9	58.1	**41.9**
NW	27.4	17.4	44.9	61.1	**38.9**
NE	26.7	18.1	44.8	59.6	**40.4**
SE	29.8	15.1	44.9	66.4	**33.6**

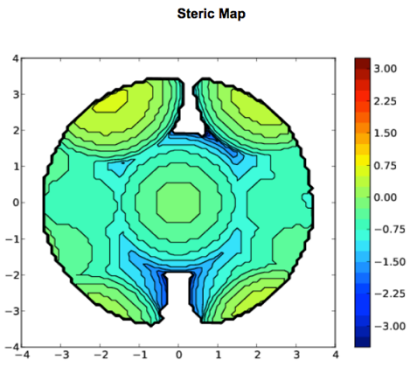


H. %VBur for **4a** with distance C-Ag normalized at 2.1 Å, sphere radius 3.5 Å.

V Free	V Buried	V Total	V Exact
110.0	69.6	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
61.3	**38.7**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	28.5	16.3	44.9	63.6	**36.4**
NW	24.9	19.9	44.9	55.6	**44.4**
NE	28.0	16.8	44.8	62.5	**37.5**
SE	28.4	16.4	44.9	63.3	**36.7**

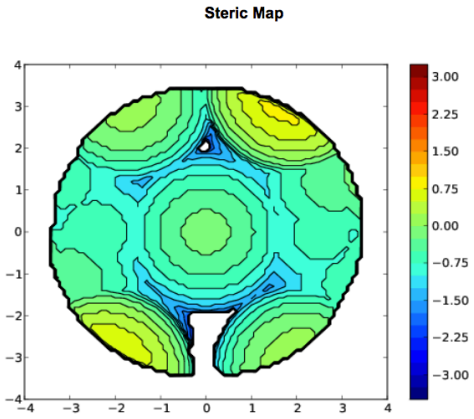


I. %VBur for **4b** with real C-Ag distance, sphere radius of 3.5 Å.

V Free	V Buried	V Total	V Exact
107.3	72.2	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
59.8	**40.2**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	26.3	18.6	44.9	58.6	**41.4**
NW	27.5	17.4	44.9	61.2	**38.8**
NE	24.8	20.0	44.8	55.4	**44.6**
SE	28.7	16.1	44.9	64.0	**36.0**

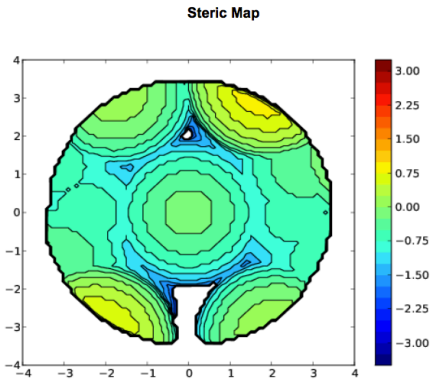


J. %VBur for **4b** with distance C-Ag normalized at 2.1 Å, sphere radius 3.5 Å.

V Free	V Buried	V Total	V Exact
106.4	73.1	179.5	179.6

%V_Free	%V_Bur	% Tot/Ex
59.3	**40.7**	100.0

Quadrant	V_f	V_b	V_t	%V_f	%V_b
SW	26.3	18.6	44.9	58.5	**41.5**
NW	27.3	17.6	44.9	60.9	**39.1**
NE	24.4	20.4	44.8	54.4	**45.6**
SE	28.4	16.4	44.9	63.4	**36.6**



V. Biological tests

Biological activity against HCT116 carcinoma cells

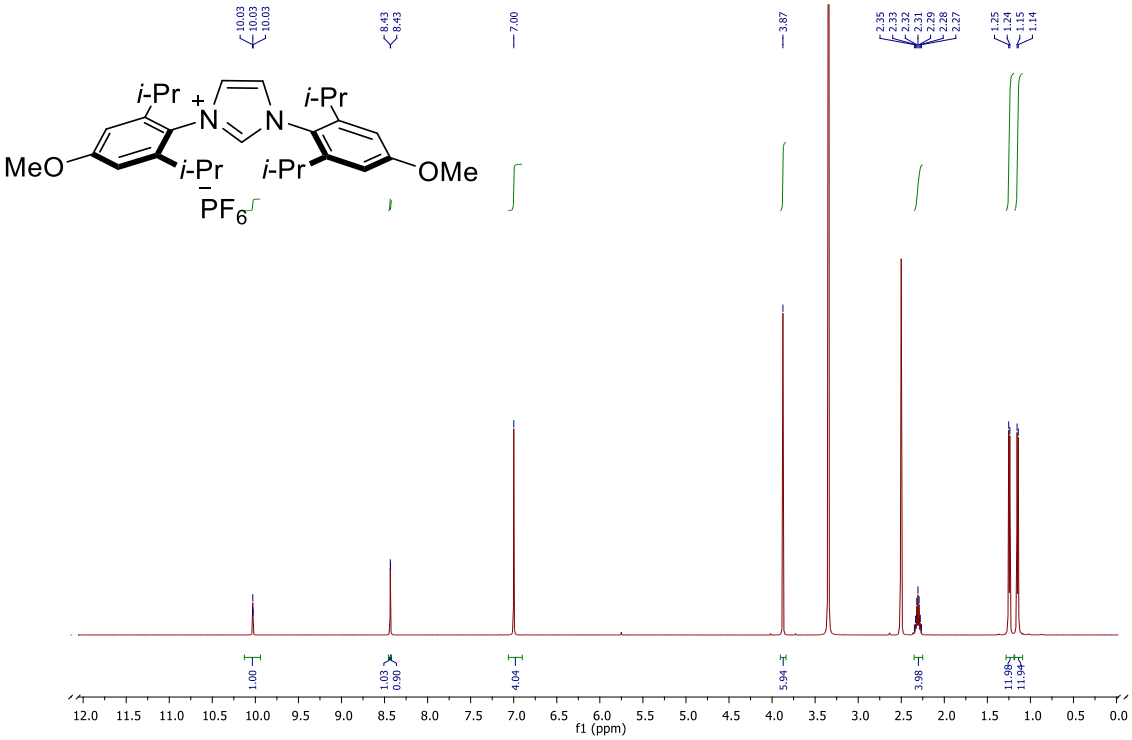
Entry	Complex	% inhibition at 10^{-5} M	% inhibition at 10^{-6} M	IC_{50} (nM)
1	**2a**	100 ± 0.1	88 ± 1	259 ± 37.3
2	**2b**	99 ± 0.1	91 ± 1	96.8 ± 2.9
3	**2c**	100 ± 0.1	88 ± 1	616 ± 5.3
4	**2d**	11 ± 2	11 ± 3	n.d.[a]
5	**2e**	8 ± 2	2 ± 1	n.d.[a]
6	**2f**	100 ± 0.1	90 ± 1	390 ± 20
7	**4a**	100 ± 0.1	83 ± 1	35.4 ± 0.9
8	**4b**	100 ± 0.1	85 ± 0.9	24.9 ± 3.2
9	**4c**	99 ± 0.3	91 ± 0.4	174 ± 48.8
10	**4f**	27 ± 1	9 ± 1	n.d.[a]
11	**4g**	98 ± 0.3	12 ± 1	2181 ± 276
12	**4h**	100 ± 1	39 ± 3	293 ± 60
13	**4i**	99 ± 0.1	8 ± 1	n.d.[a]
14	**4j**	86 ± 0.6	87 ± 1	140 ± 10
15	**5a**	93 ± 0.2	88 ± 0.6	35.6 ± 2
16	**5b**	86 ± 0.2	89 ± 1	42.2 ± 2.4
17	**5c**	76 ± 4	23 ± 5	n.d.[a]
18	**5d**	95 ± 0.6	86 ± 1	21 ± 1.6
19	**5e**	99 ± 0.1	40 ± 5	n.d.[a]
20	**5f**	100 ± 0.1	71 ± 3	163 ± 44
21	Doxorubicin			810 ± 110
22	cisplatin			5370 ± 150

[a] n.d.= not determined.

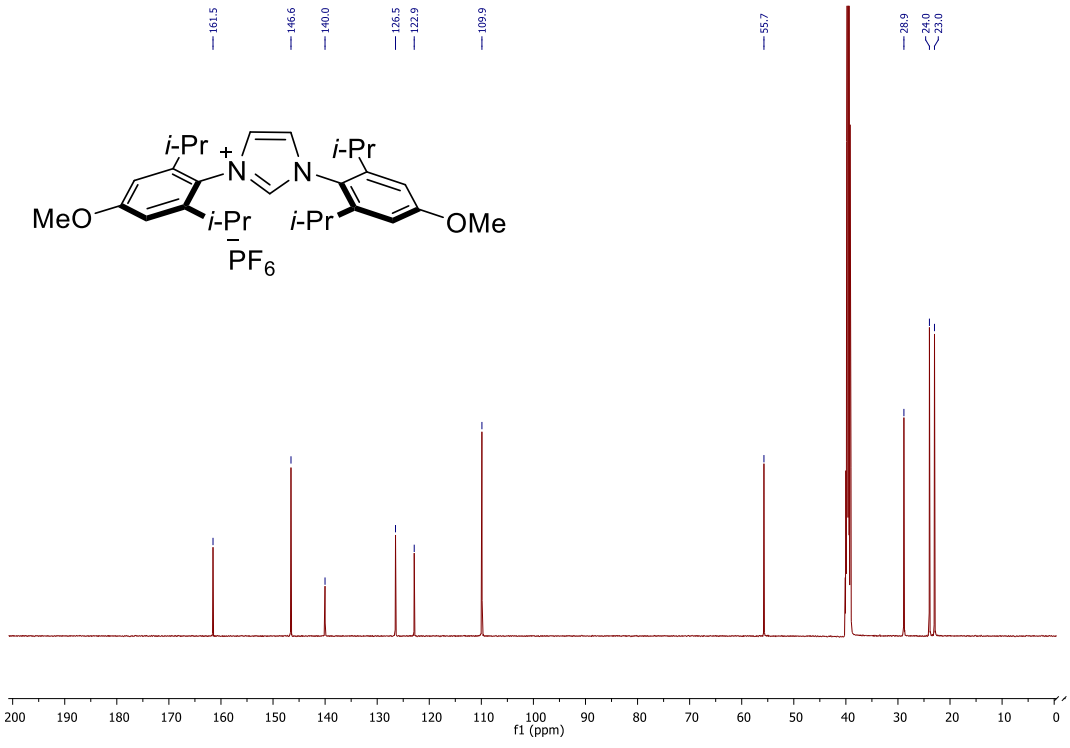
VI. NMR SPECTRA

[1,3-Bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium hexafluorophosphate 3a

^{1}H NMR (500 MHz, DMSO-d_6)

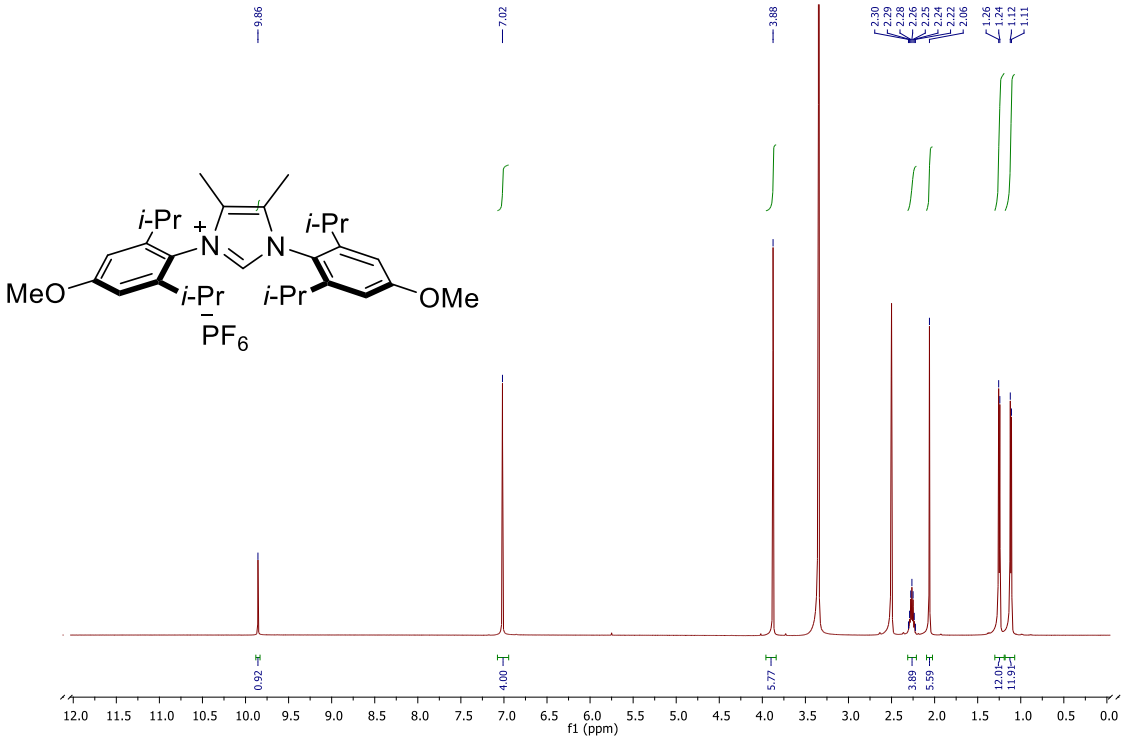


^{13}C NMR (126 MHz, DMSO-d_6)

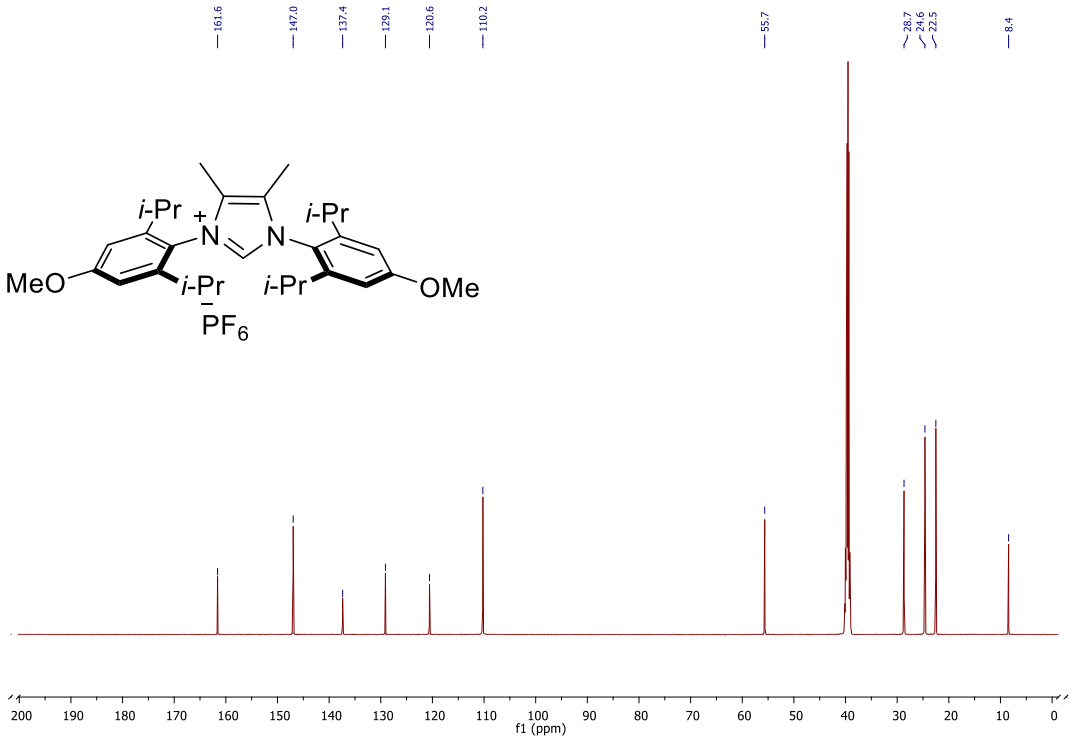


[4,5-Dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazolium hexafluorophosphate 3b

^{1}H NMR (500 MHz, DMSO-d_6)

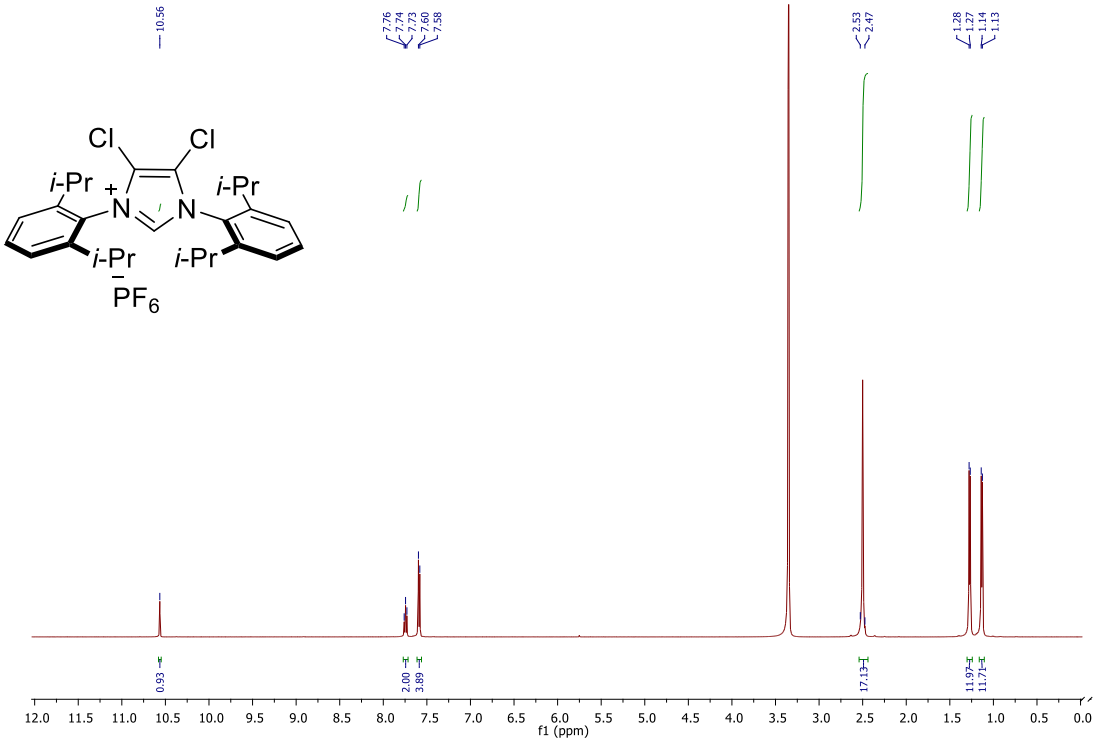


^{13}C NMR (126 MHz, DMSO-d_6)

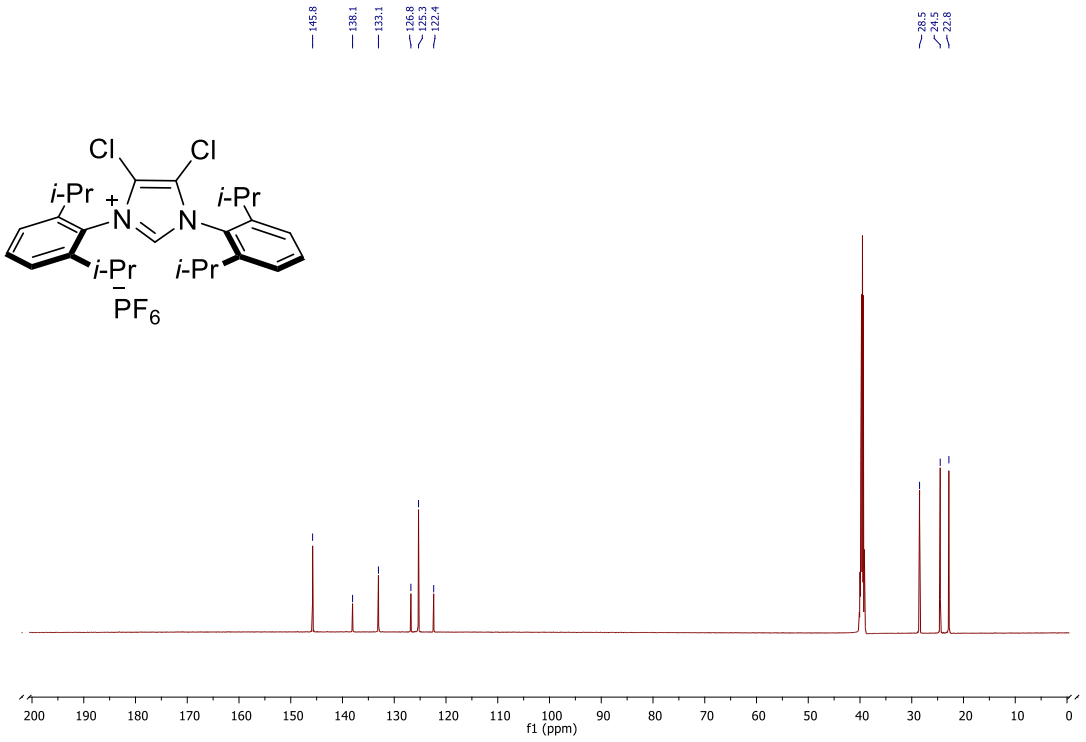


[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazolium hexafluorophosphate 3c

^{1}H NMR (500 MHz, DMSO-d_6)

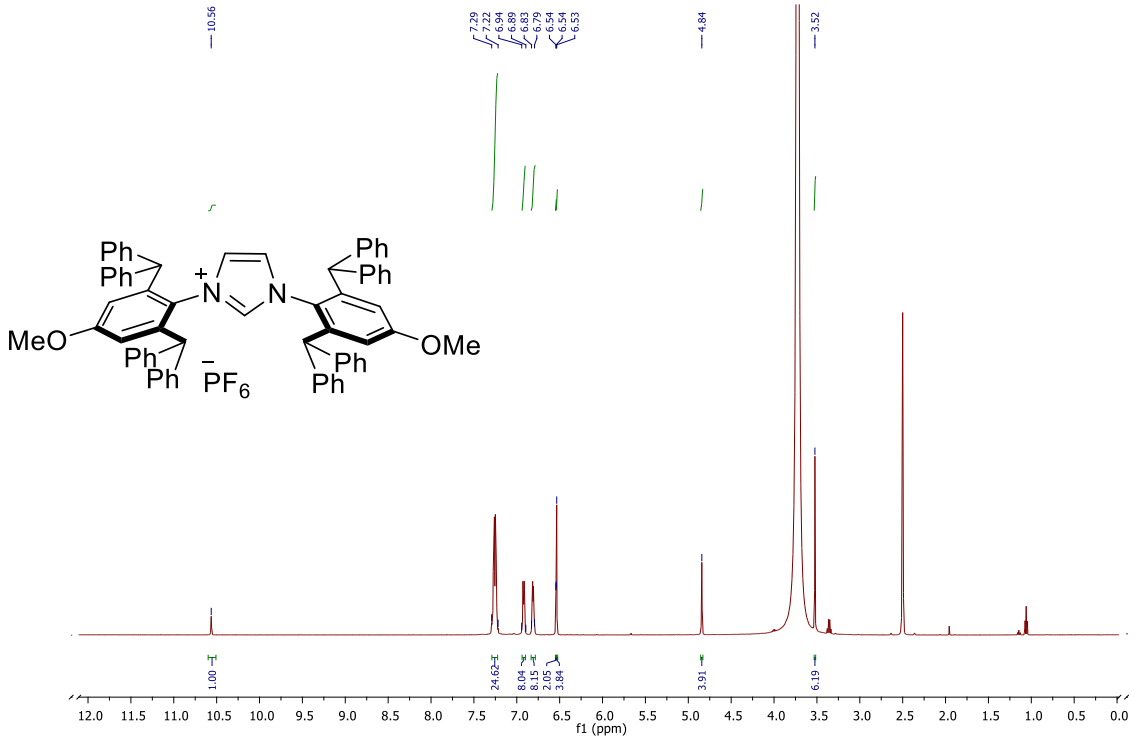


^{13}C NMR (126 MHz, DMSO-d_6)

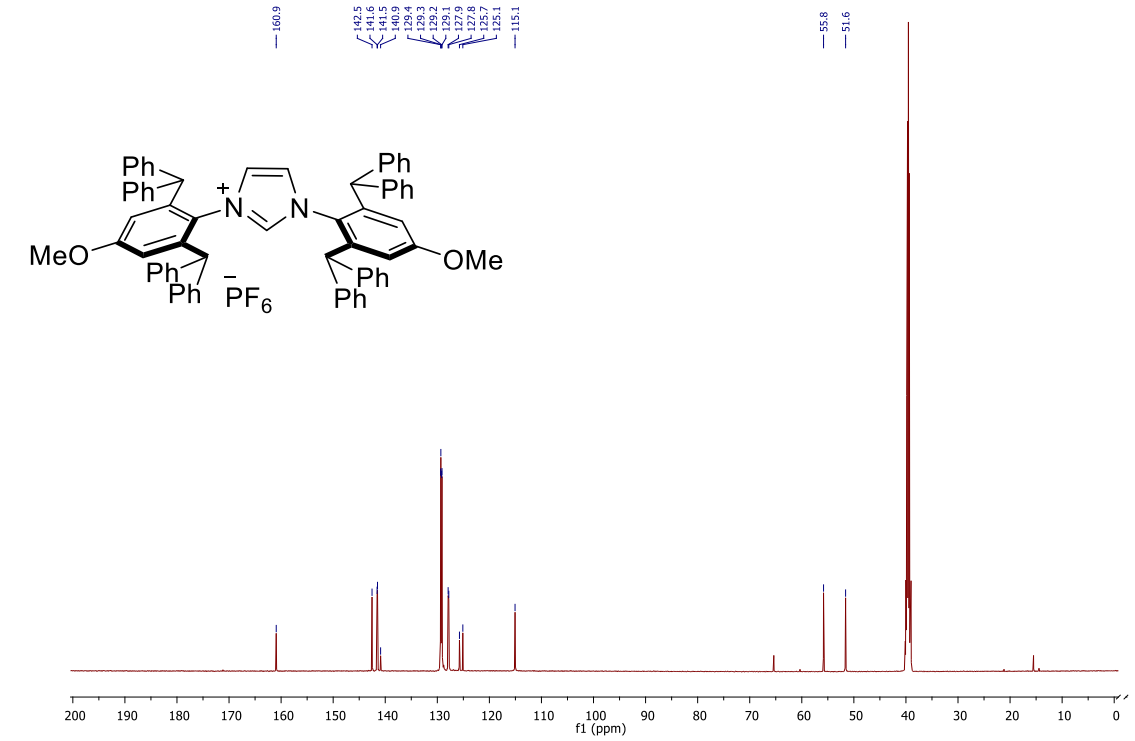


[1,3-Bis(4-methoxy-2,6-diphenyl)phenyl]imidazolium hexafluorophosphate 3d

^{1}H NMR (500 MHz, DMSO-d_6)

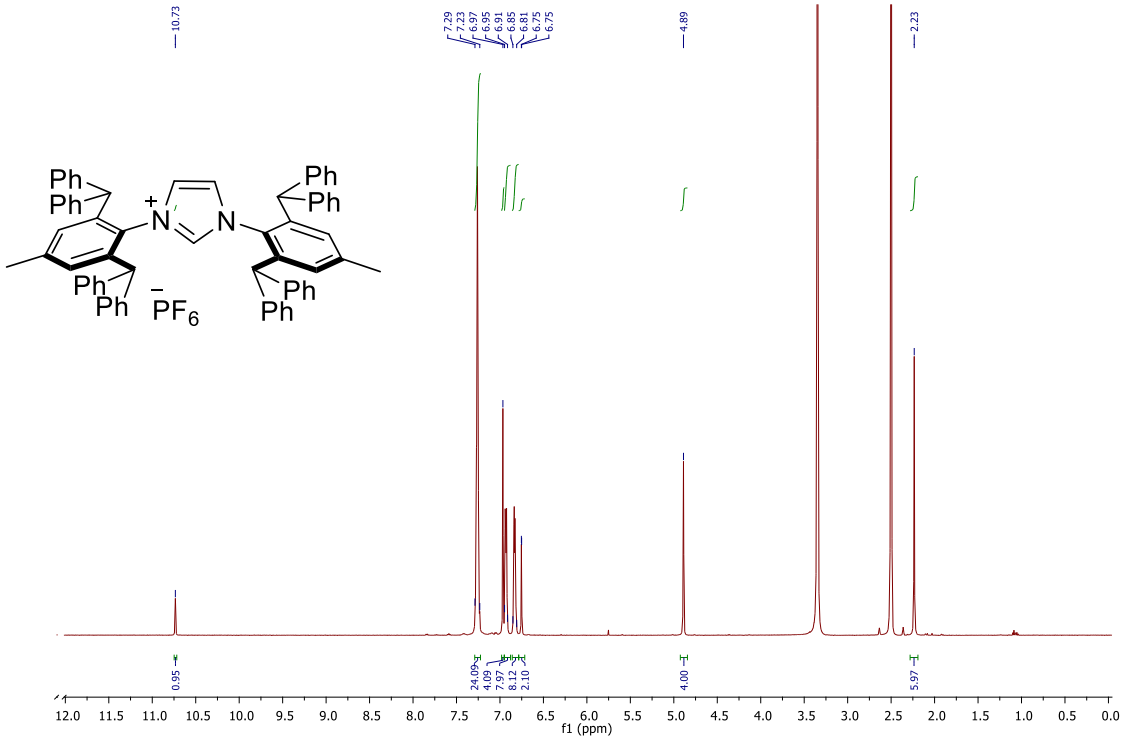


^{13}C NMR (126 MHz, DMSO-d_6)

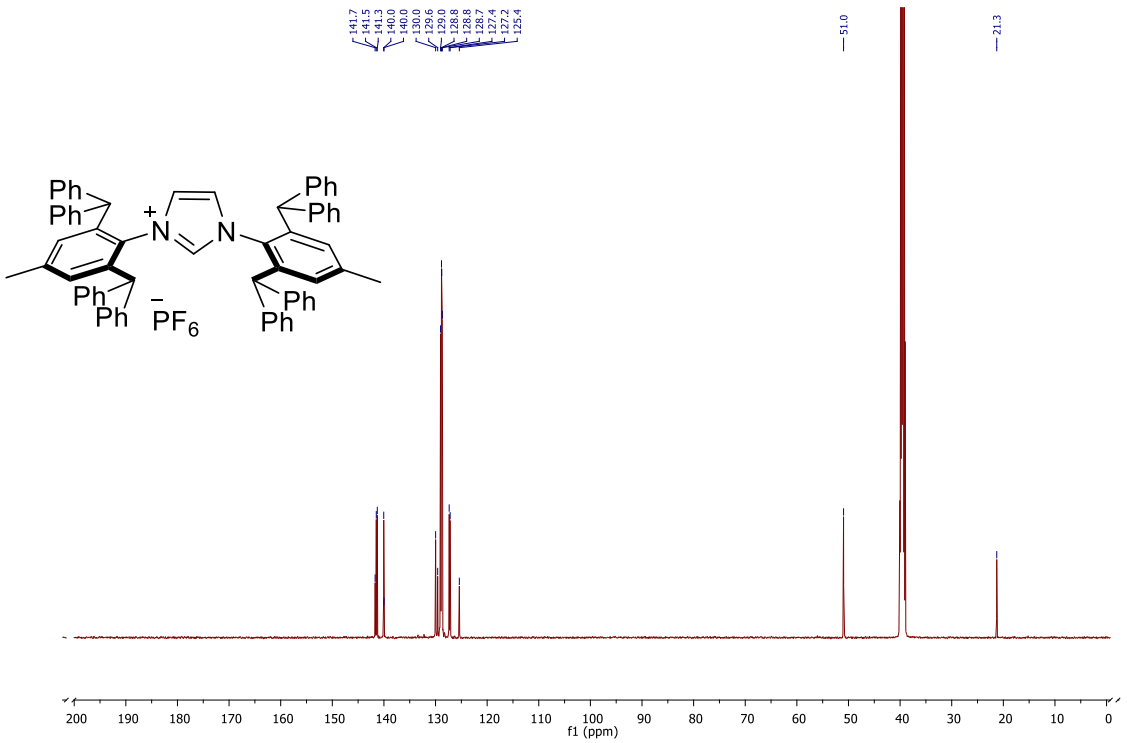


[1,3-Bis(4-methyl-2,6-diphenyl)phenyl]imidazolium hexafluorophosphate 3e

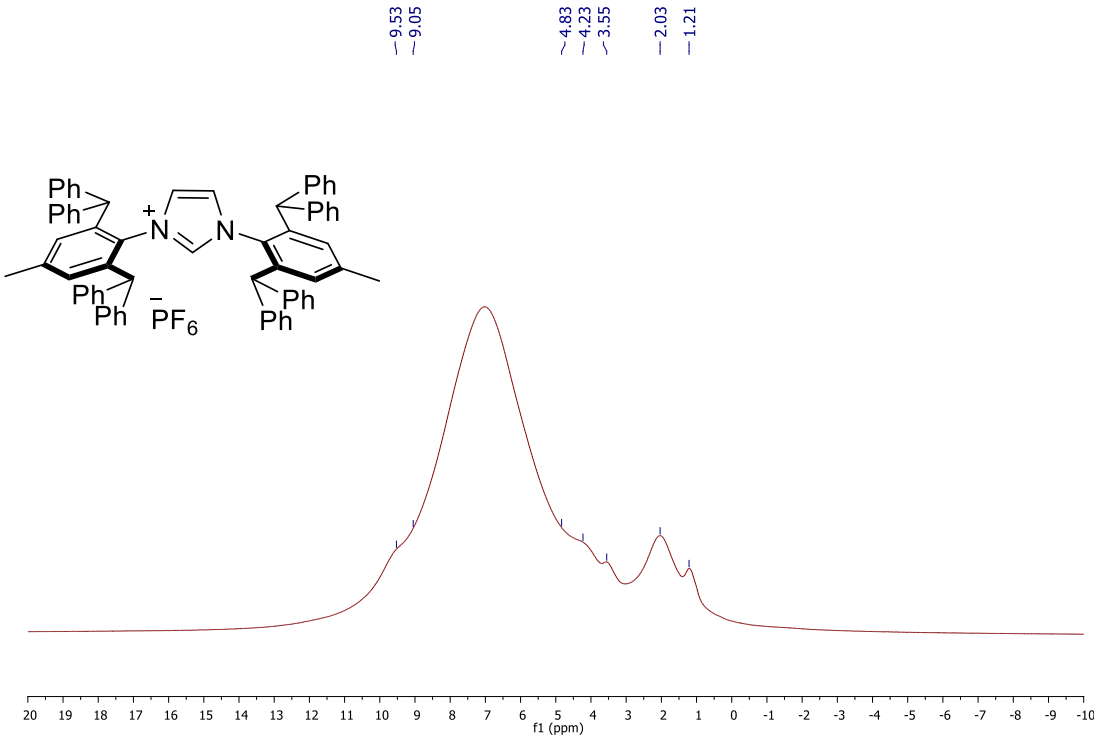
^{1}H NMR (500 MHz, DMSO-d_6)



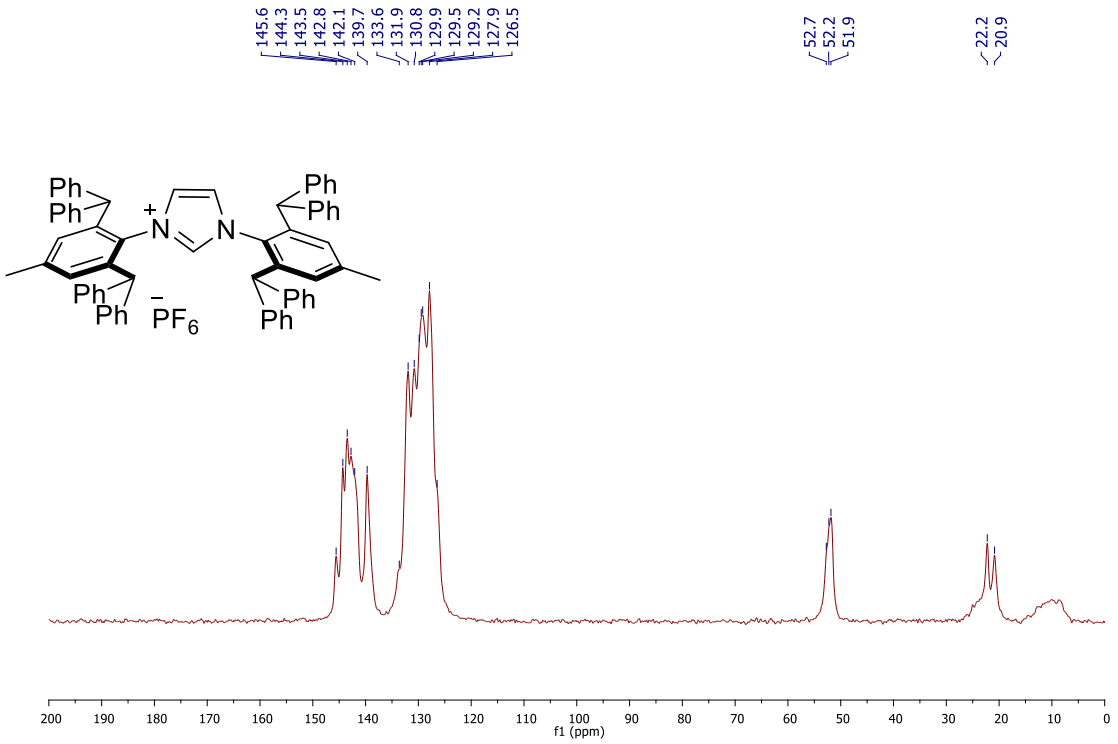
^{13}C NMR (126 MHz, DMSO-d_6)



^{1}H solid state HR-MAS NMR (600 MHz)

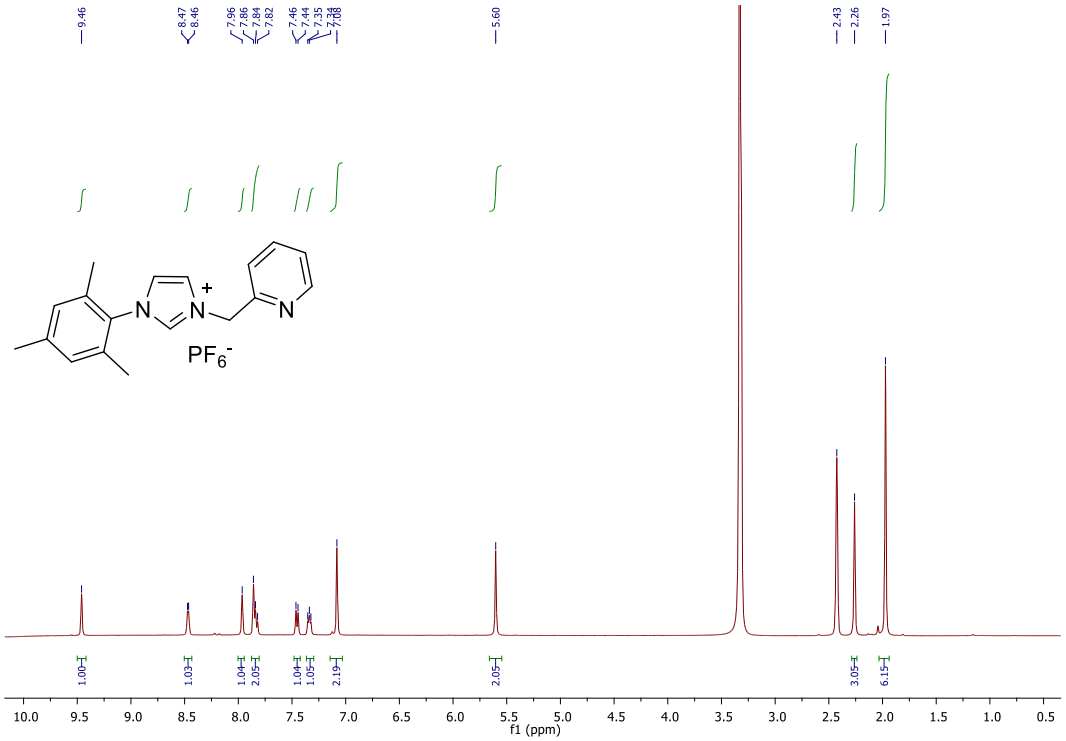


^{13}C solid state HR-MAS NMR (151 MHz)

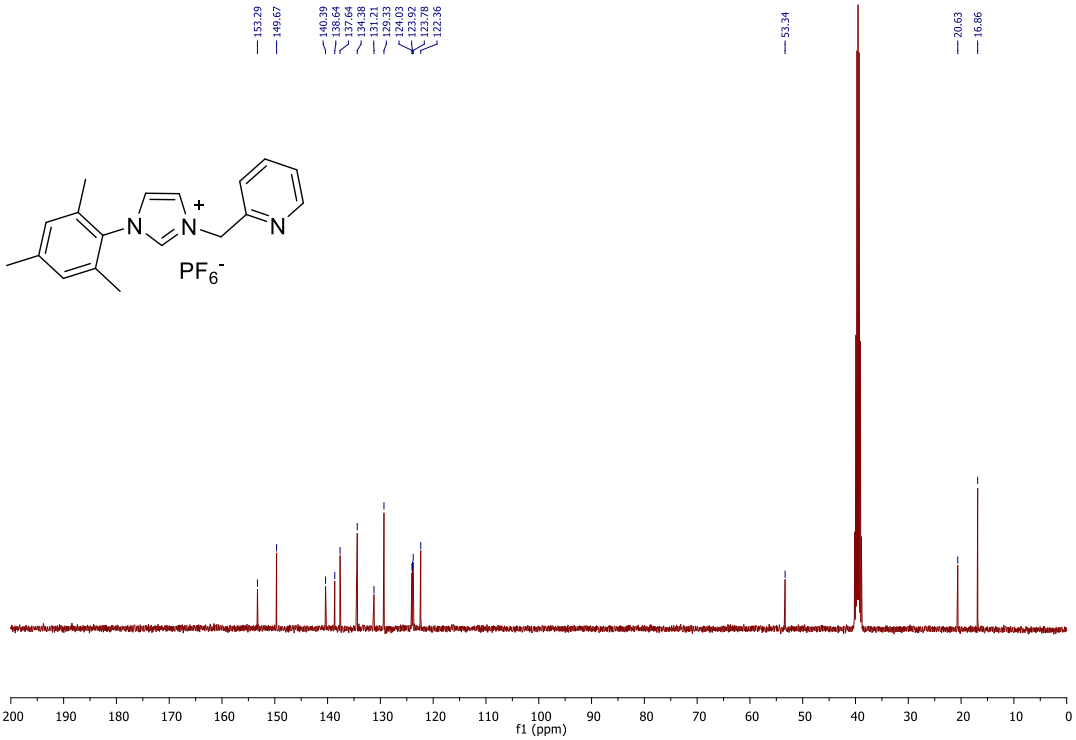


1-mesityl-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium hexafluorophosphate(V) 3f

^{1}H NMR (400 MHz, DMSO-d_6)

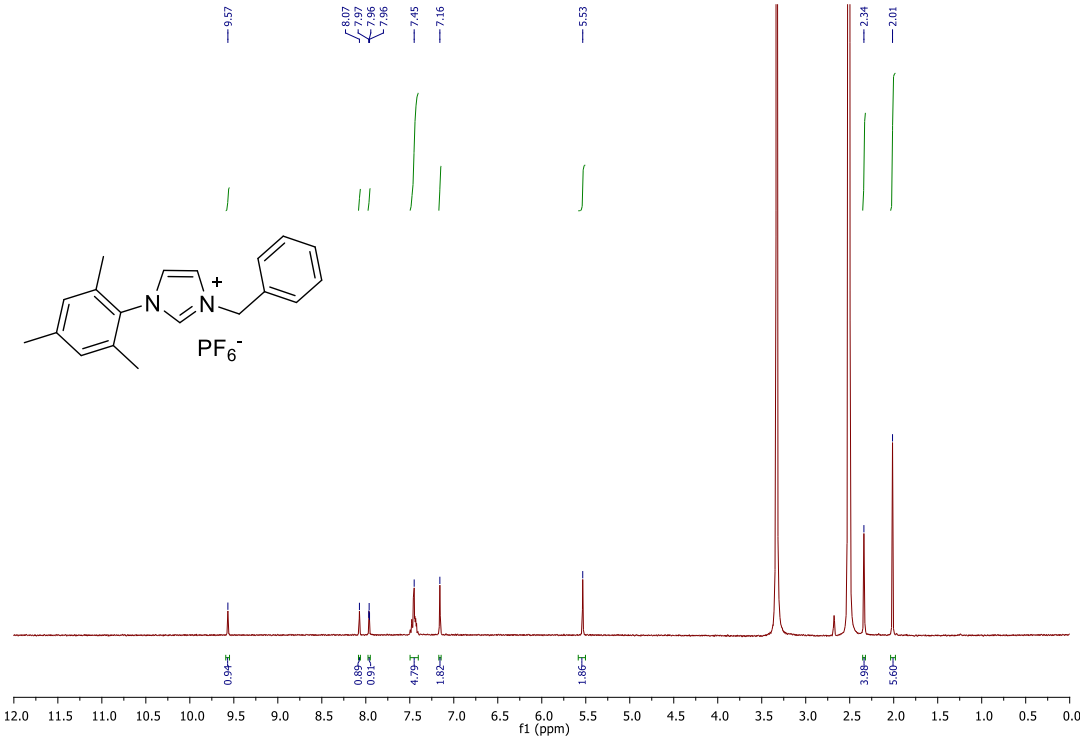


^{13}C NMR (101 MHz, DMSO-d_6)

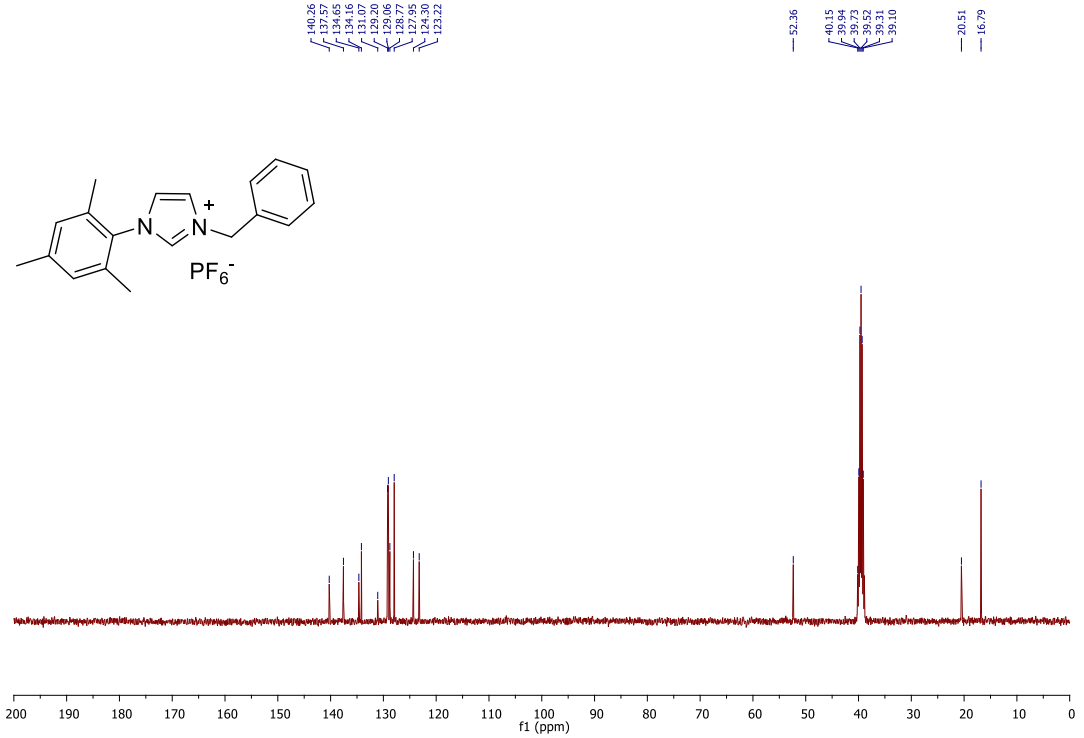


1-Benzyl-3-mesitylimidazolium hexafluorophosphate(V) 3g

^{1}H NMR (400 MHz, DMSO-d_6)

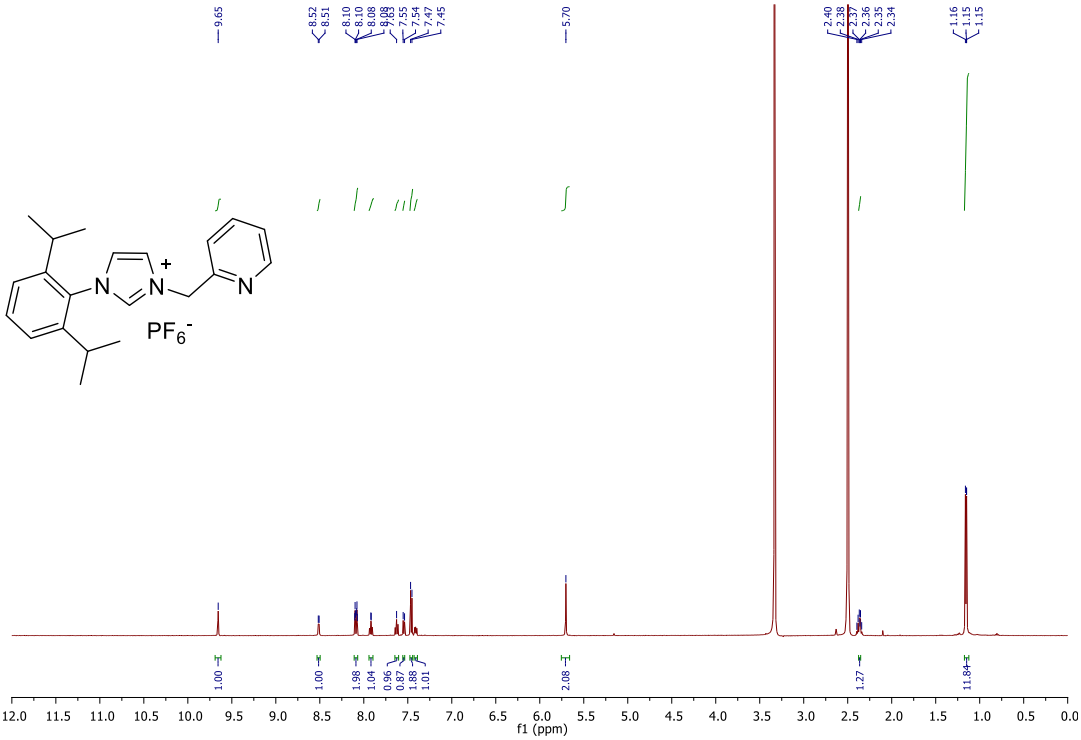


^{13}C NMR (101 MHz, DMSO-d_6)

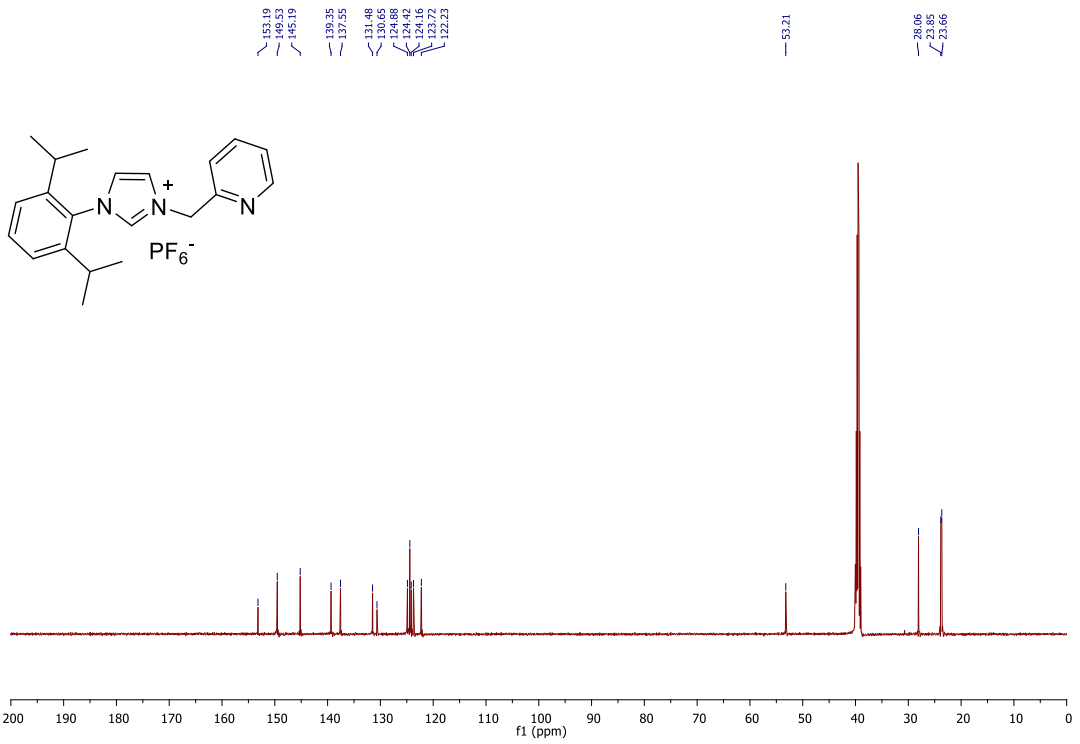


1-(2,6-diisopropylphenyl)-3-(pyridin-2-ylmethyl)-1H-imidazol-3-ium hexafluorophosphate(V) 3h

^{1}H NMR (500 MHz, DMSO-d_6)

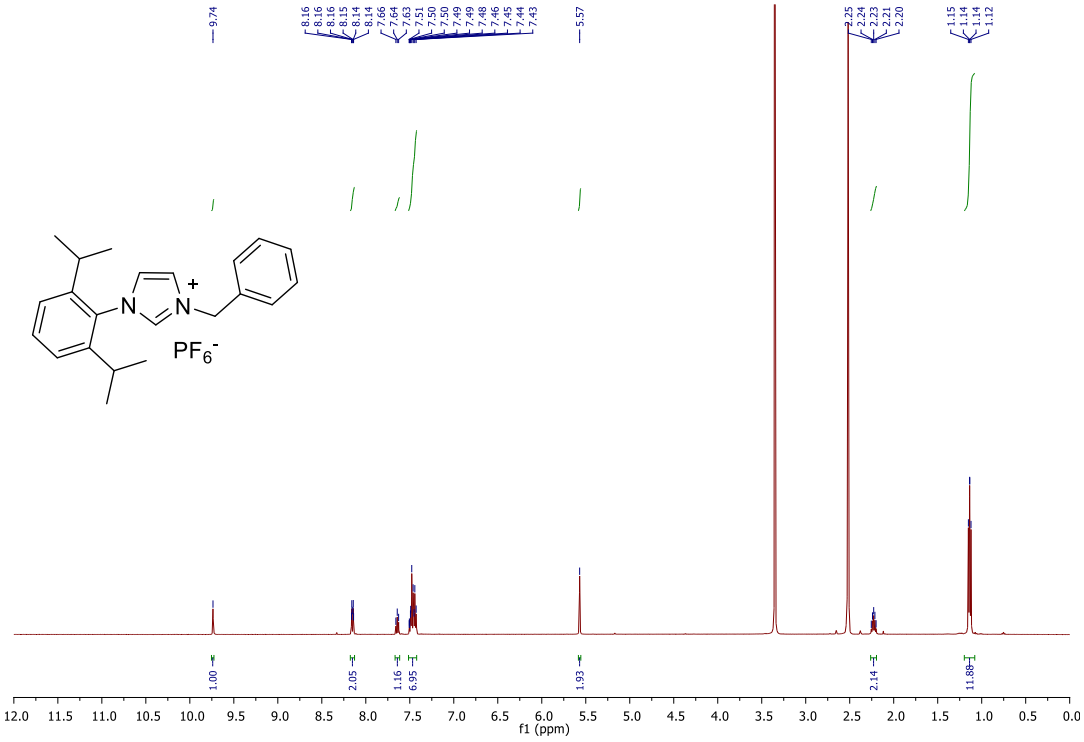


^{13}C NMR (125 MHz, DMSO-d_6)

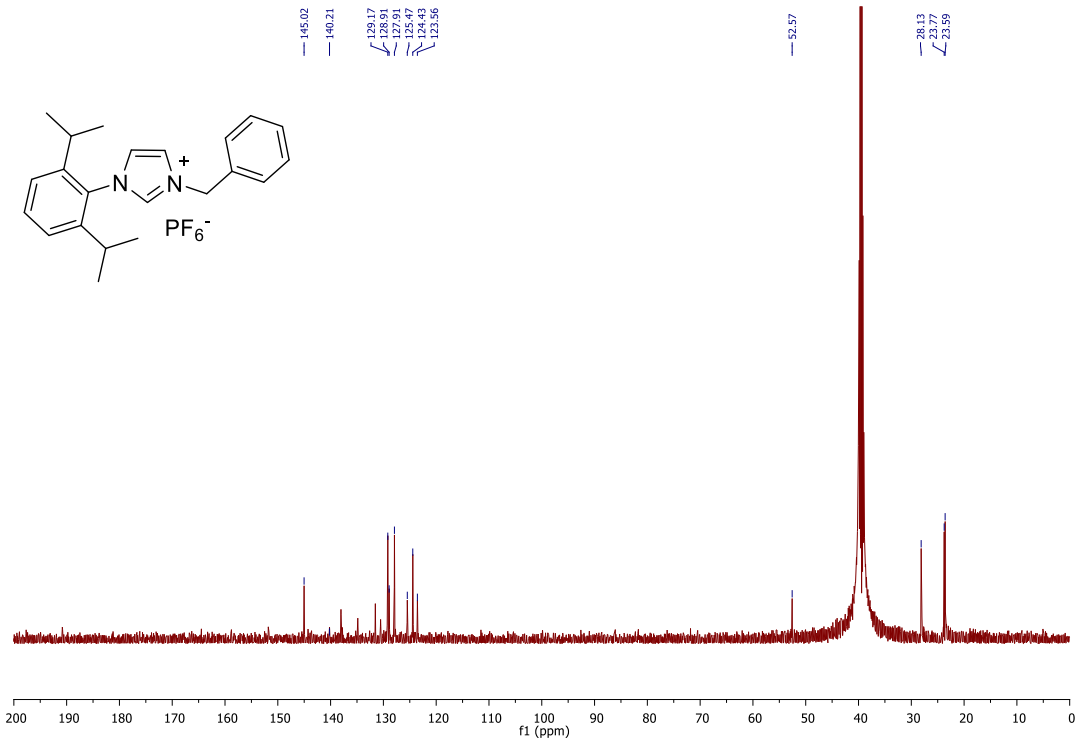


3-benzyl-1-(2,6-diisopropylphenyl)-1H-imidazol-3-ium hexafluorophosphate(V) 3i

^{1}H NMR (500 MHz, DMSO-d_6)

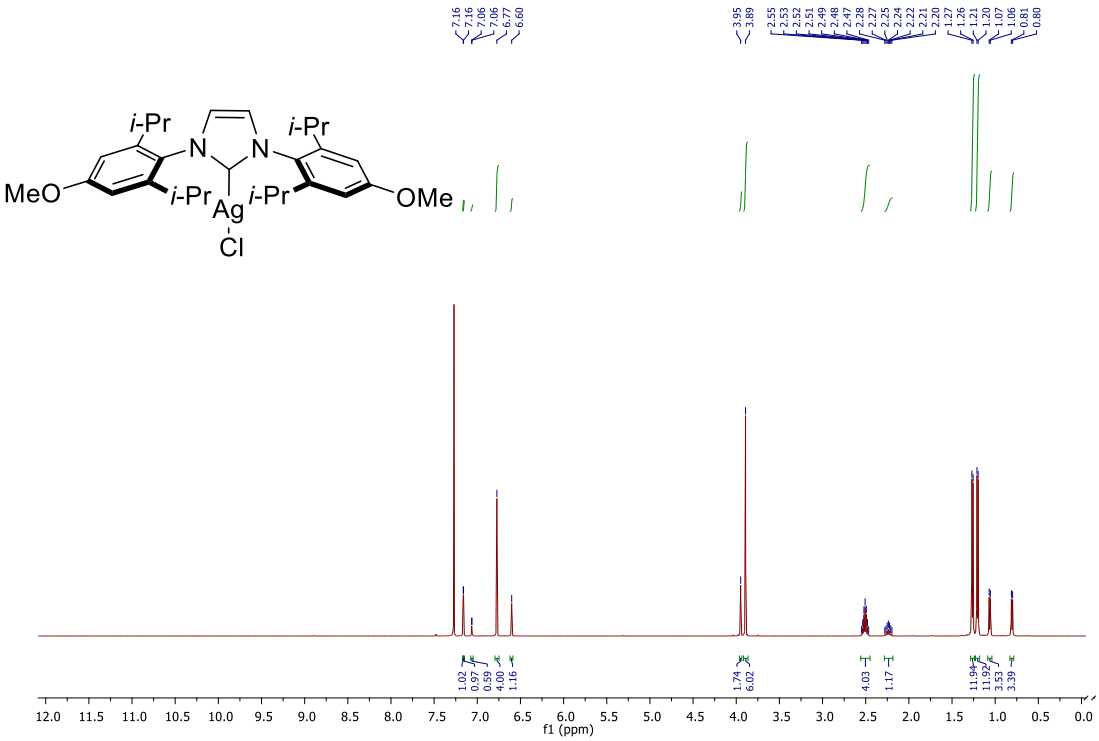


^{13}C NMR (125 MHz, DMSO-d_6)

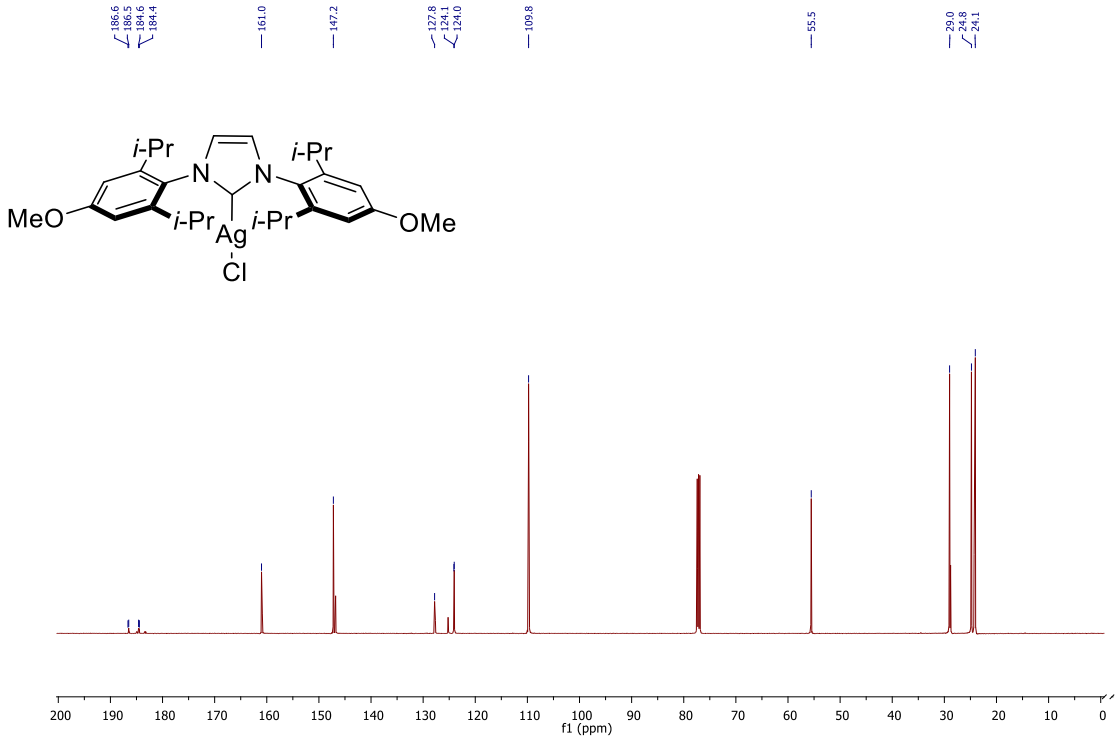


[[1,3-Bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazol-2-ylidene]silver chloride 2a

^{1}H NMR (500 MHz, $CDCl_3$)

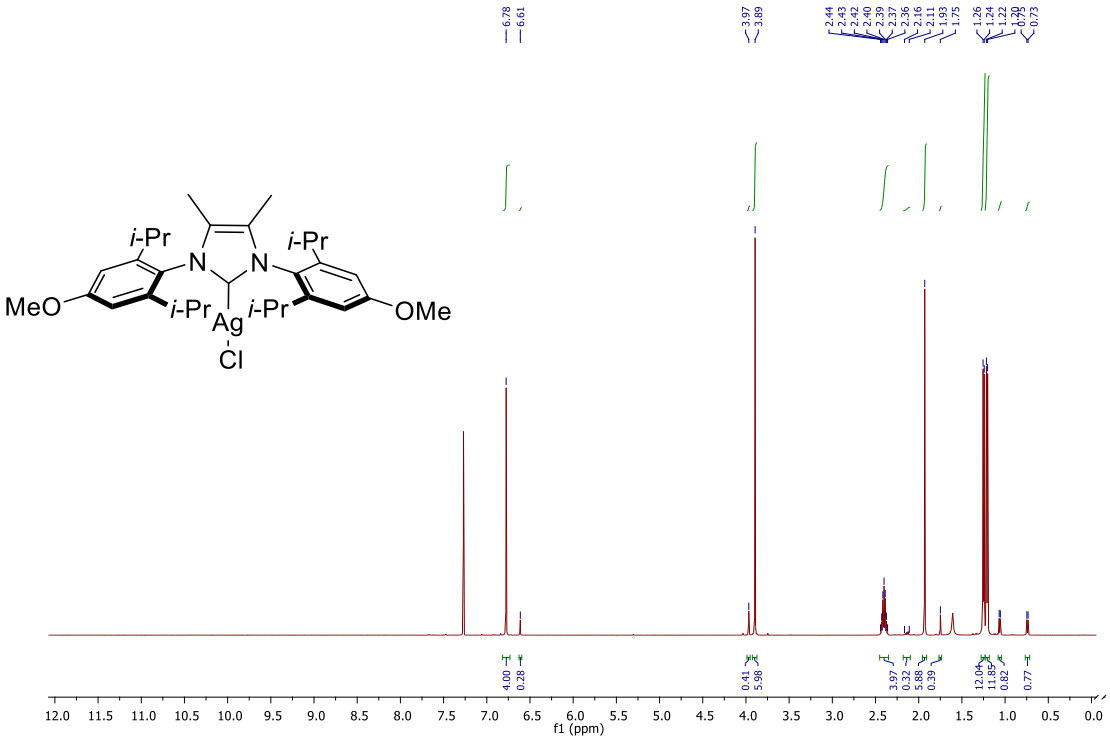


^{13}C NMR (126 MHz, $CDCl_3$)

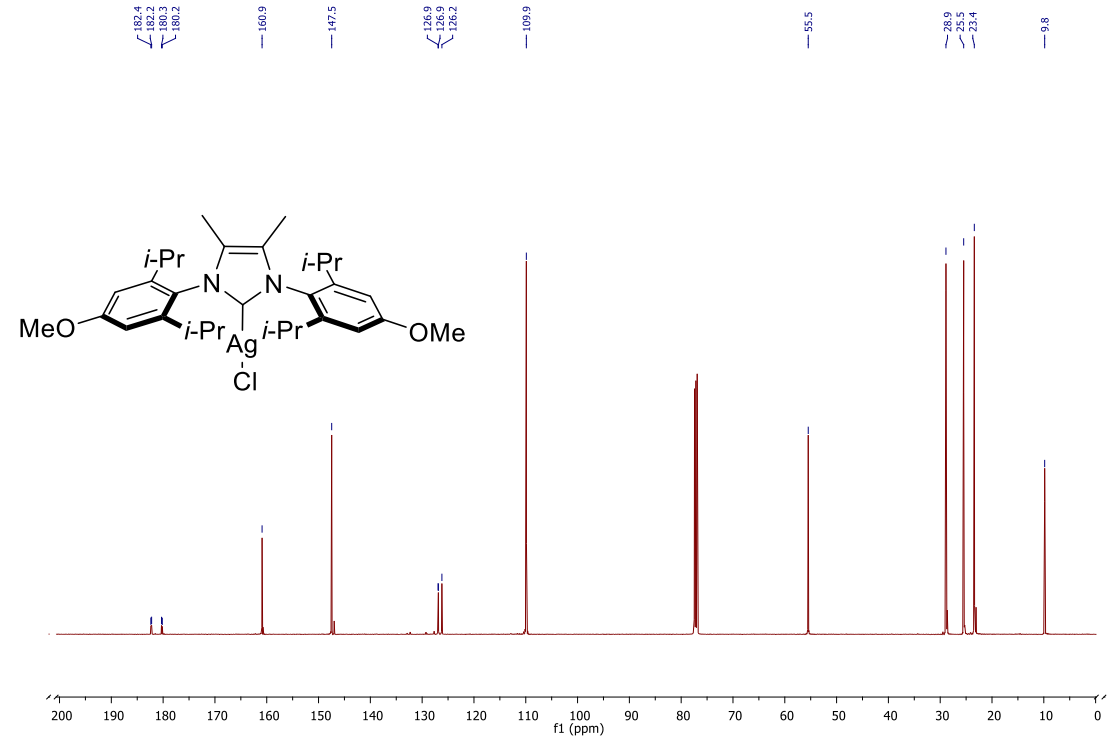


[[4,5-Dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazol-2-ylidene]silver chloride 2b

^{1}H NMR (500 MHz, $CDCl_3$)

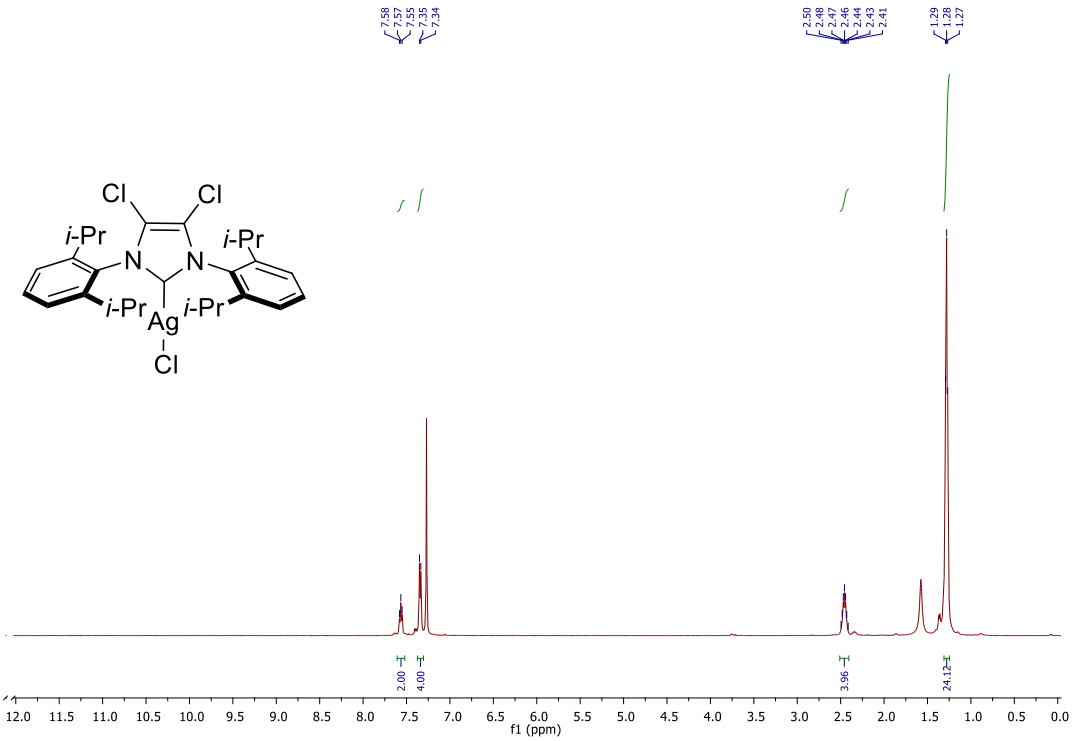


^{13}C NMR (126 MHz, $CDCl_3$)

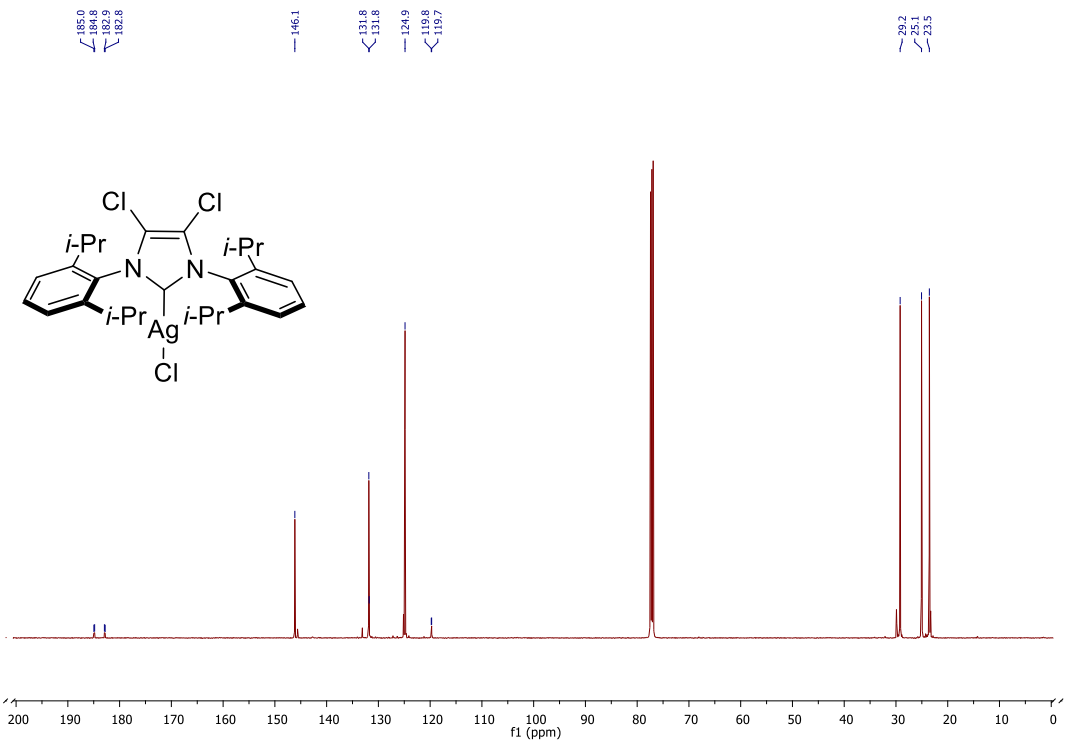


[[1,3-Bis(2,6-di*iso*propylphenyl)-4,5-dichloro]imidazol-2-ylidene]silver chloride 2c

^{1}H NMR (500 MHz, $CDCl_3$)

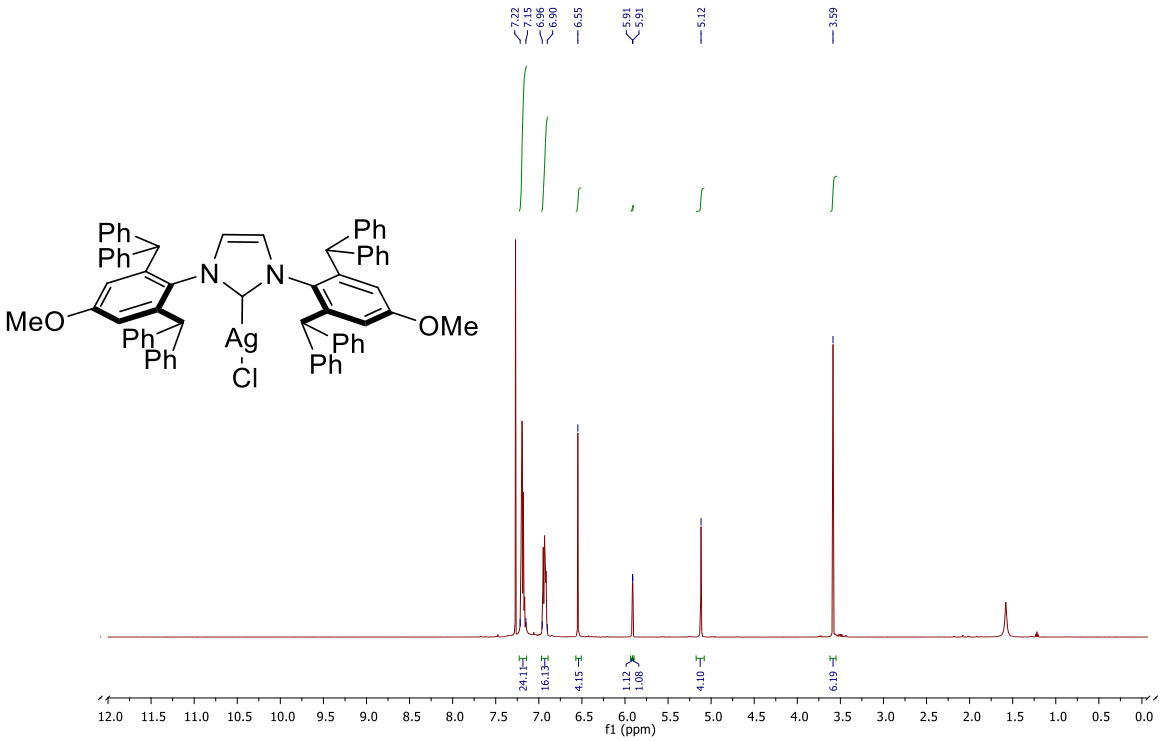


^{13}C NMR (126 MHz, $CDCl_3$)

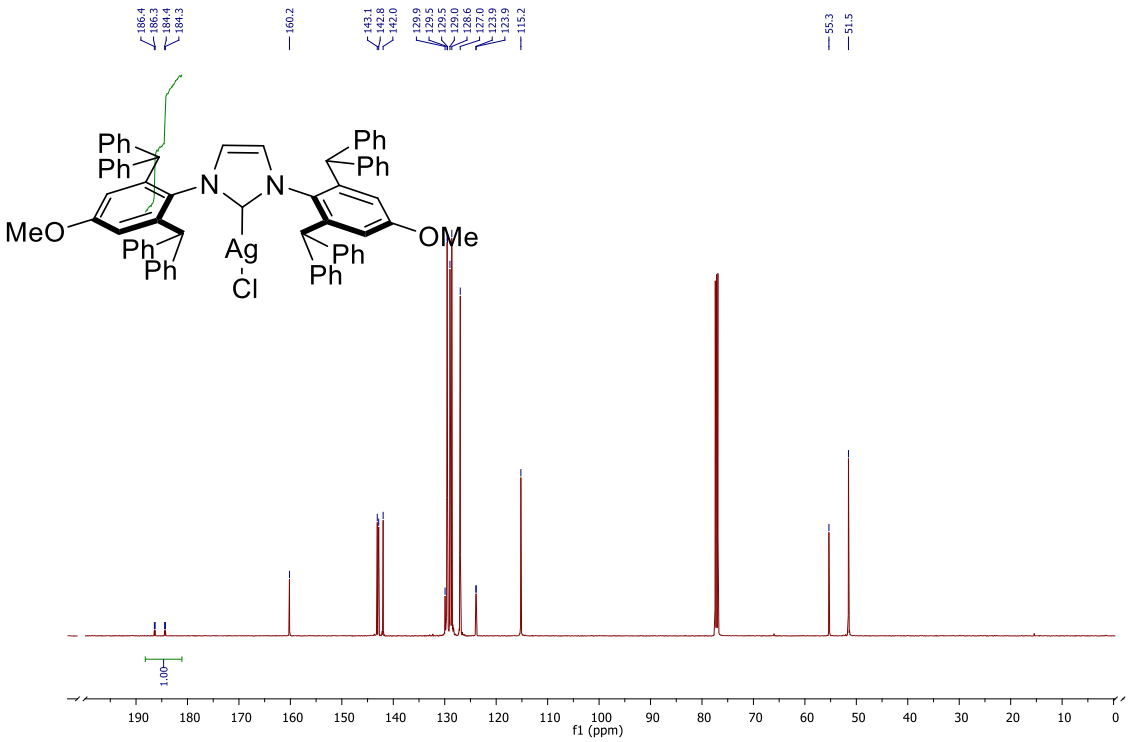


[[1,3-Bis(4-methoxy-2,6-diphenyl)phenyl]imidazol-2-ylidene]silver chloride 2d

^{1}H NMR (500 MHz, $CDCl_3$)

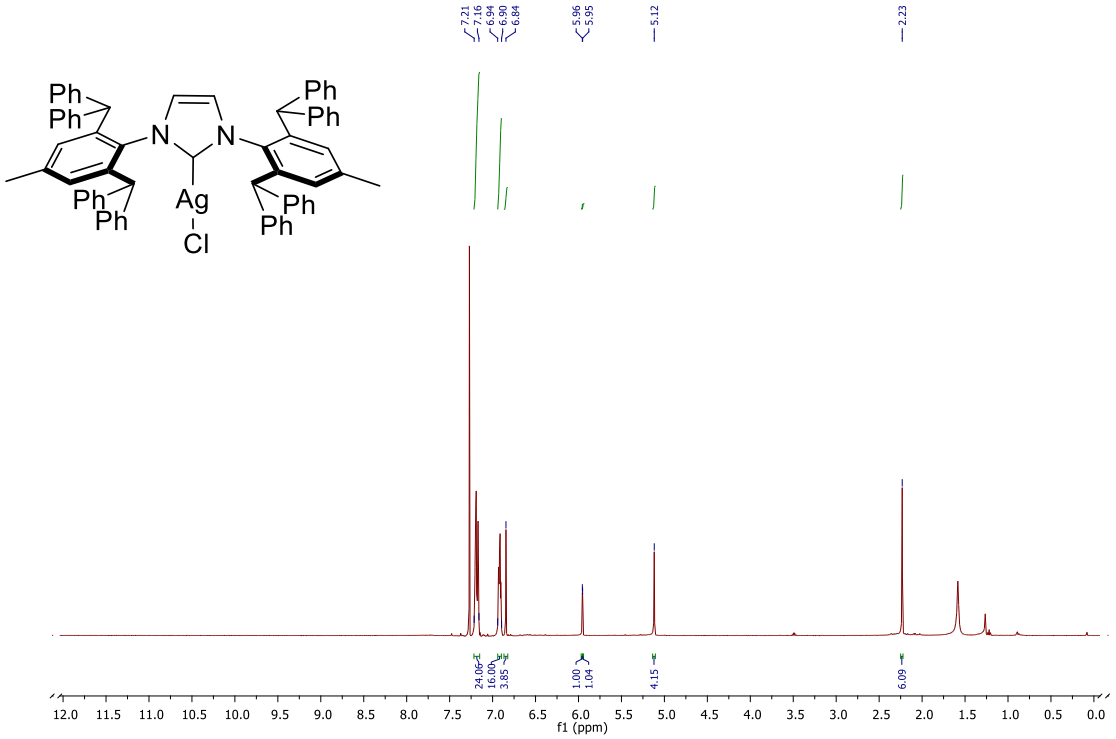


^{13}C NMR (126 MHz, $CDCl_3$)

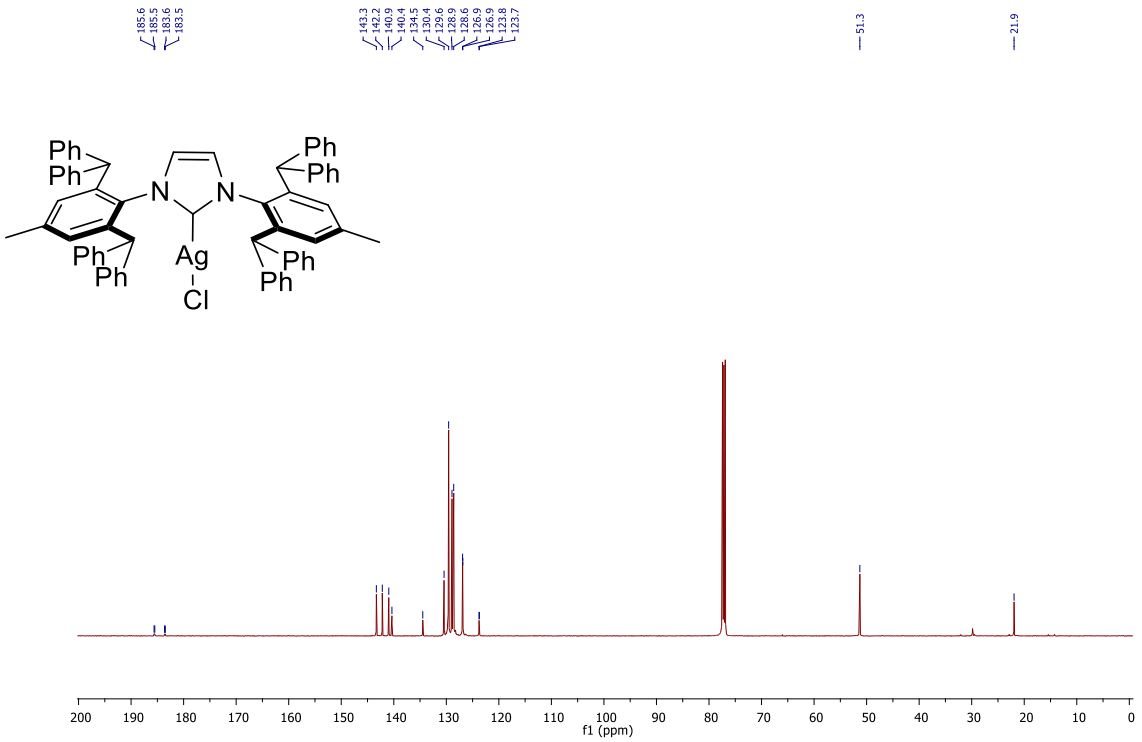


[[1,3-Bis(4-methyl-2,6-diphenyl)phenyl]imidazol-2-ylidene]silver chloride 2e

^{1}H NMR (500 MHz, $CDCl_3$)

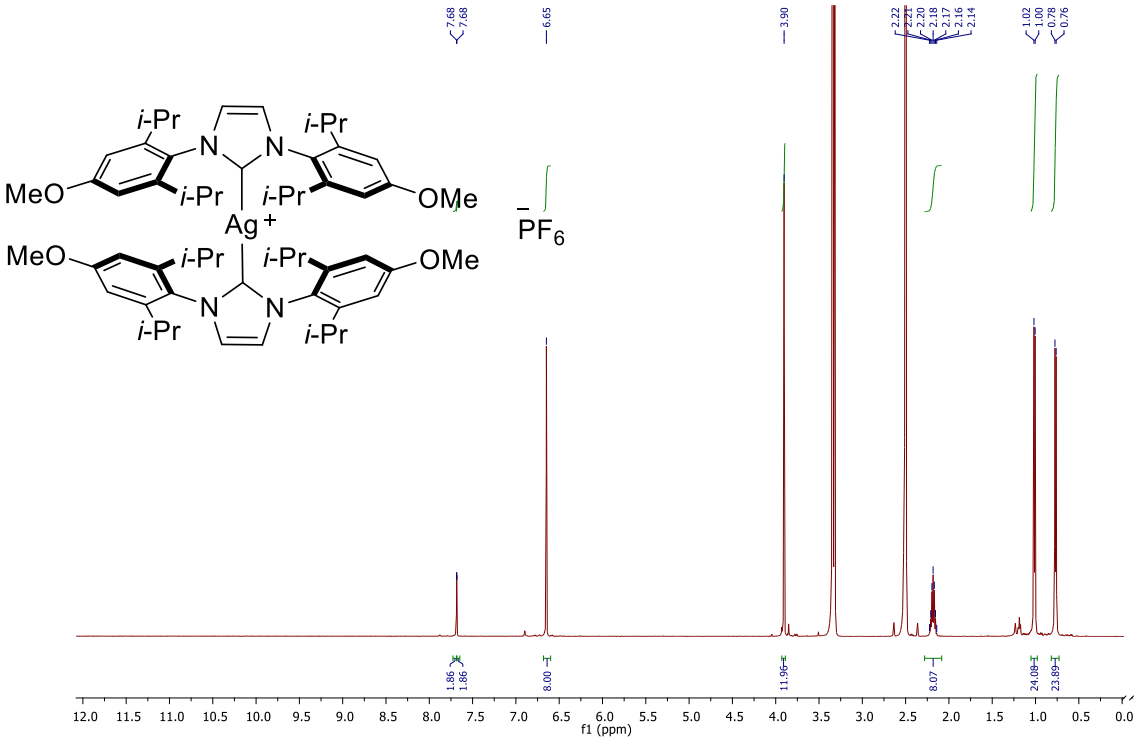


^{13}C NMR (126 MHz, $CDCl_3$)

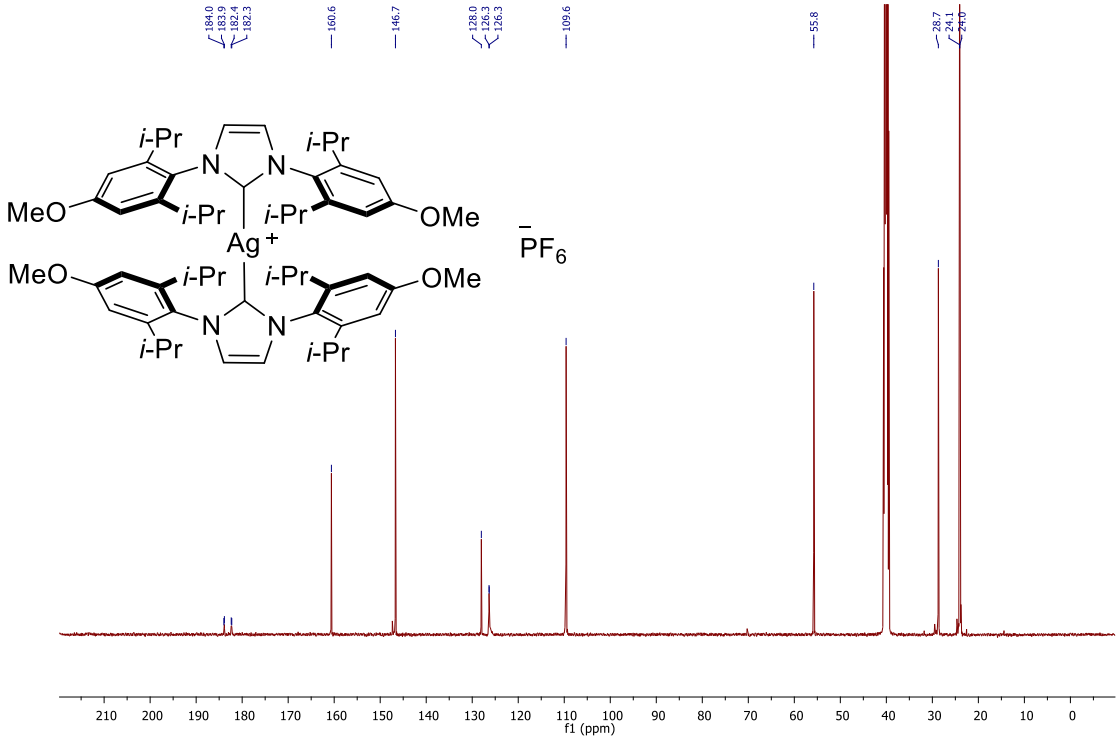


Bis[(1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl]imidazol-2-ylidene]silver hexafluorophosphate 4a

^{1}H NMR (500 MHz, DMSO-d_6)

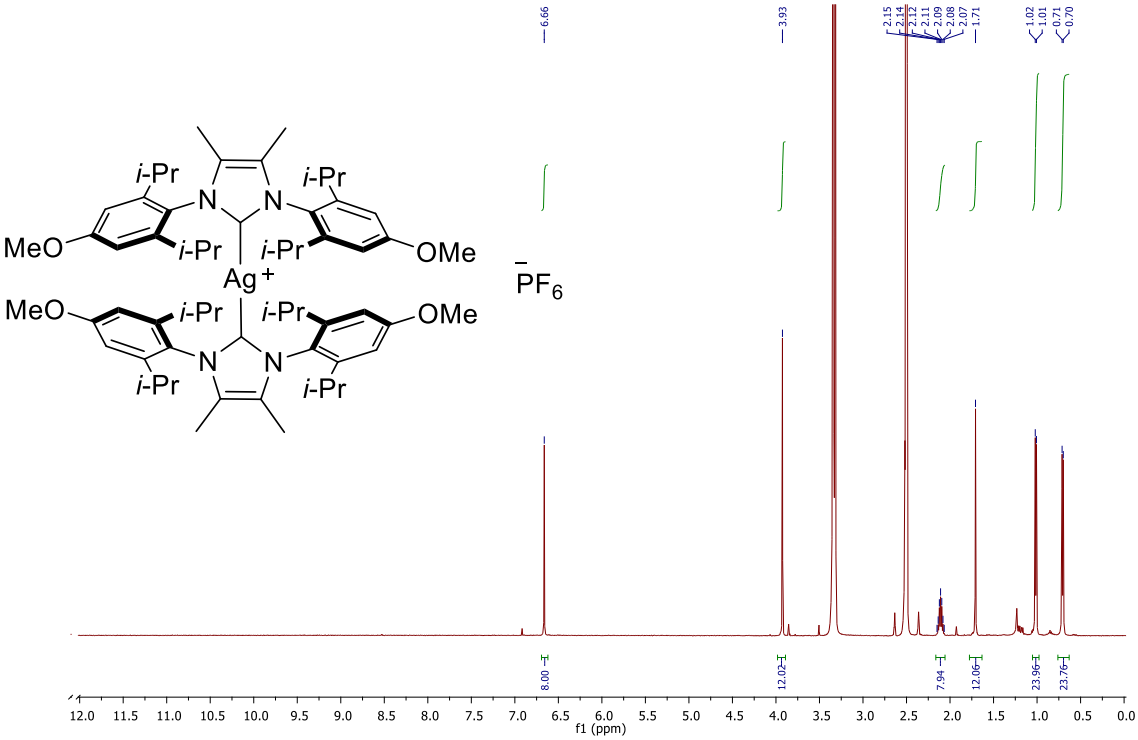


^{13}C NMR (126 MHz, DMSO-d_6)

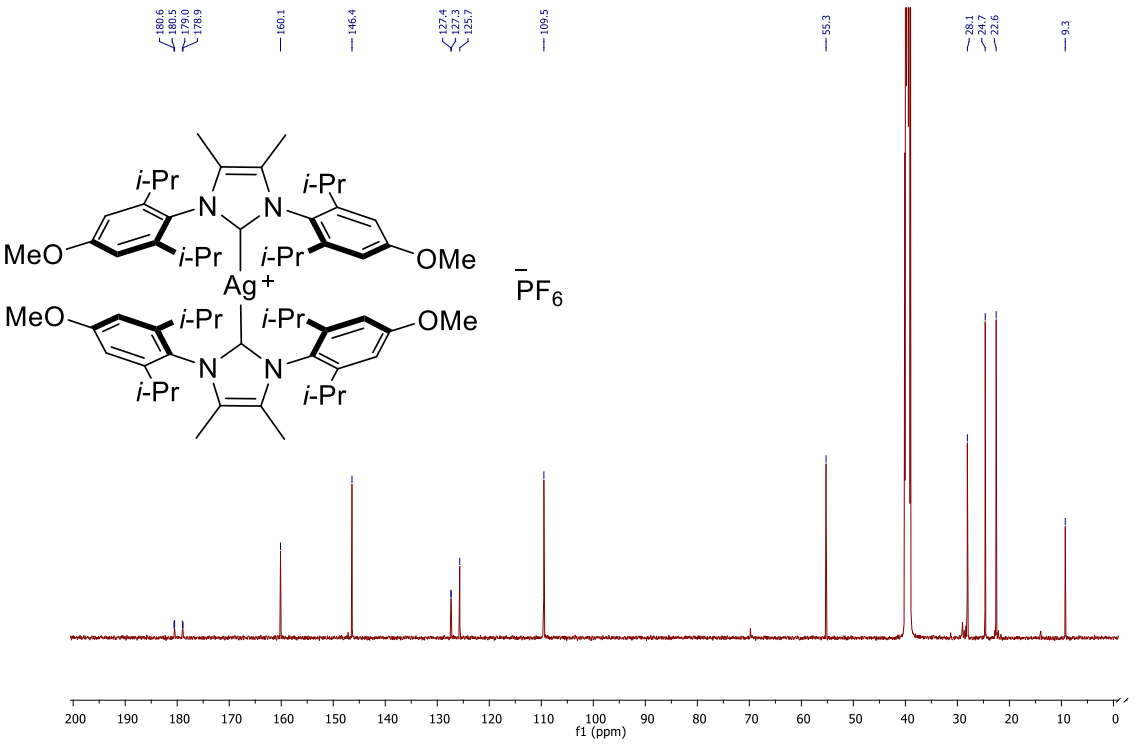


Bis[(4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl)imidazole-2-ylidene]silver hexafluorophosphate 4b

^{1}H NMR (500 MHz, DMSO-d_6)

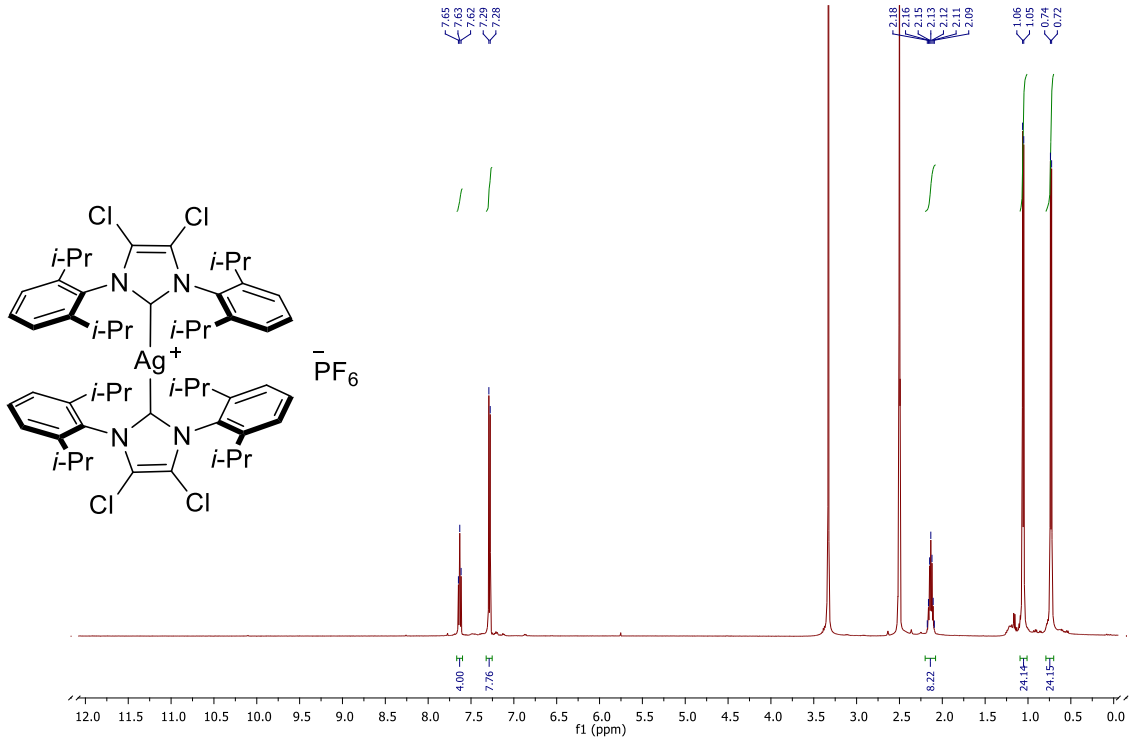


^{13}C NMR (126 MHz, DMSO-d_6)

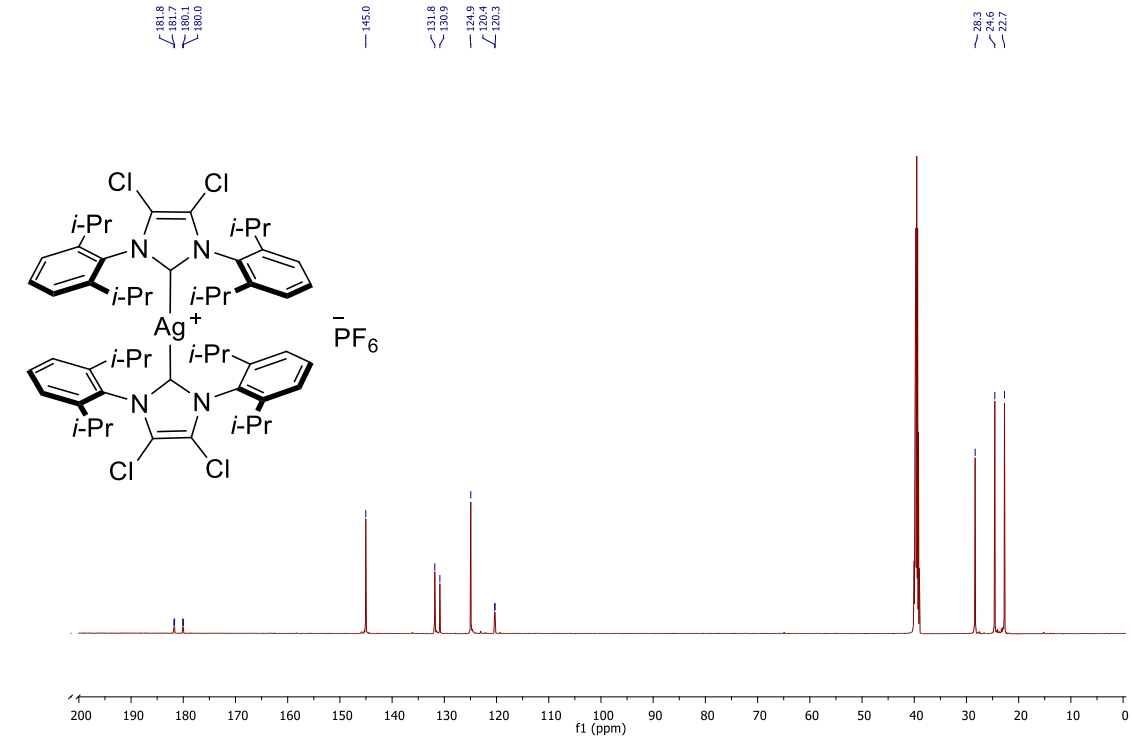


Bis[(1,3-bis(2,6-di*iso*propylphenyl)-4,5-dichloro)imidazol-2-ylidene] silver hexafluorophosphate 4c

^{1}H NMR (500 MHz, DMSO-d_6)

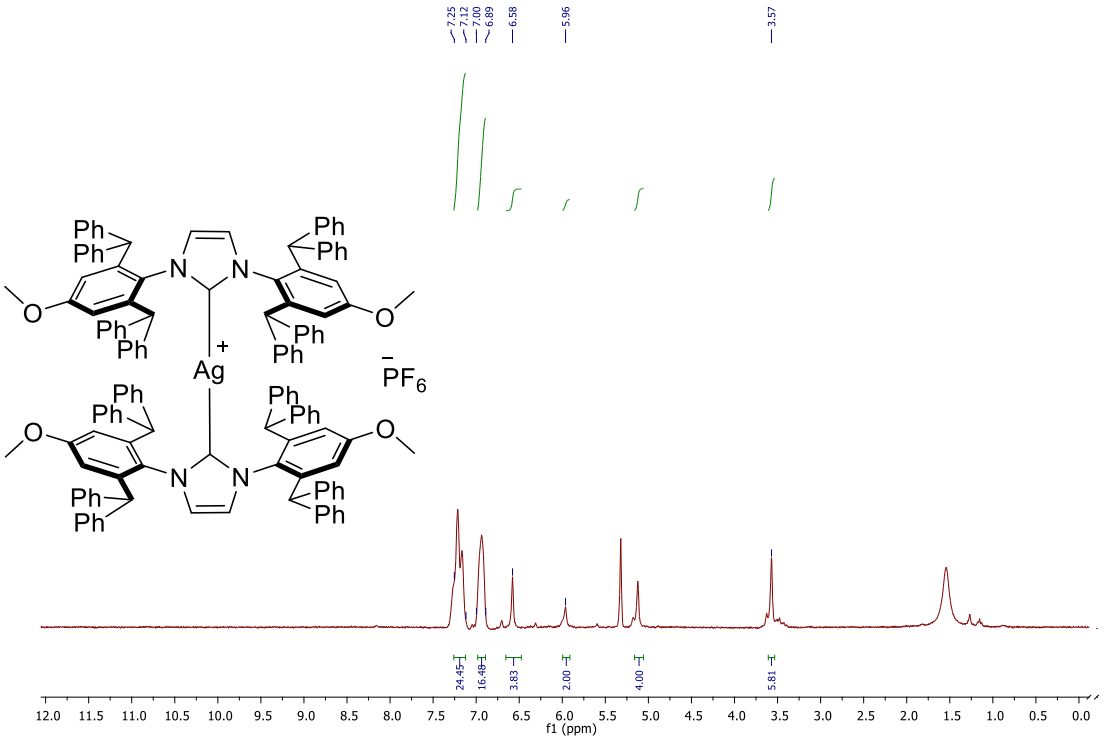


^{13}C NMR (126 MHz, DMSO-d_6)

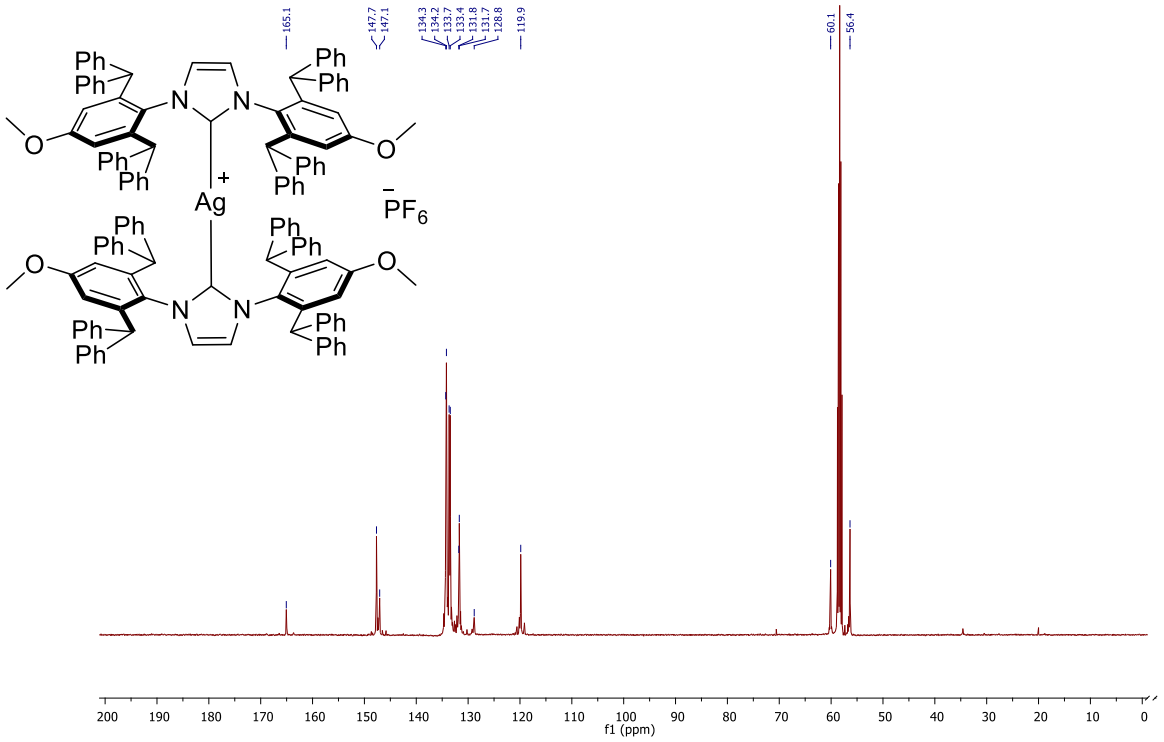


Bis[(1,3-bis(4-methoxy-2,6-diphenyl)phenyl)imidazol-2-ylidene]silver hexafluorophosphate 4d

^{1}H NMR (300 MHz, CD_2Cl_2)

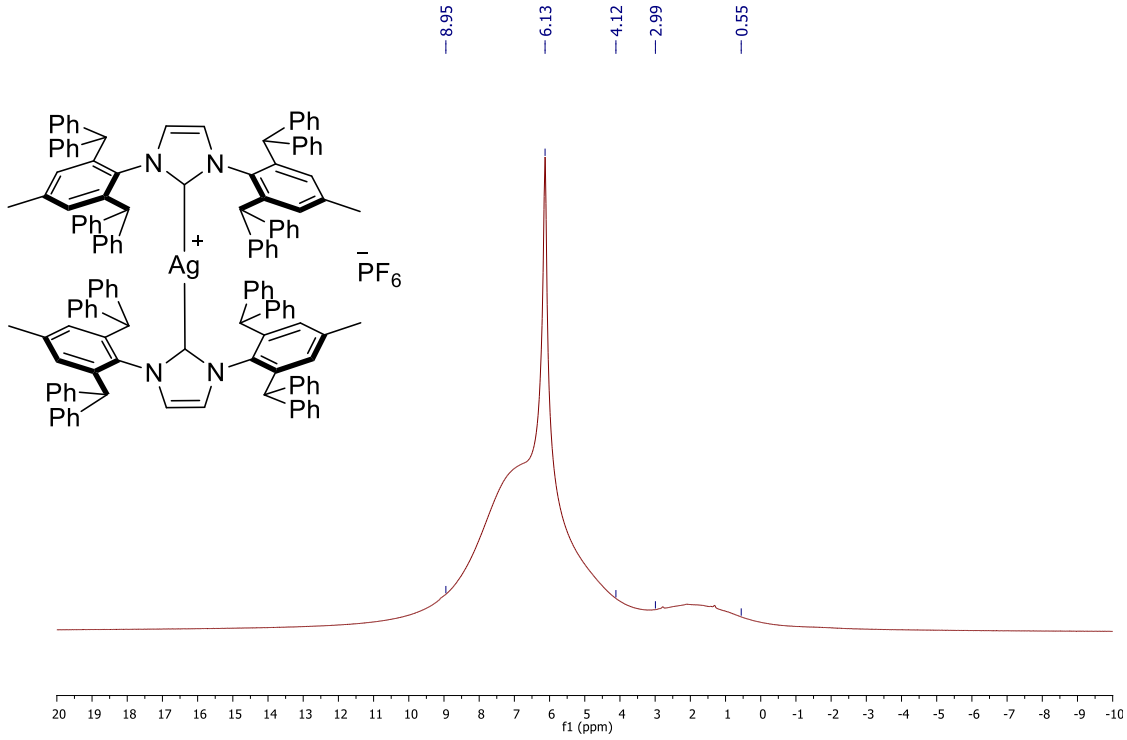


^{13}C NMR (126 MHz, CD_2Cl_2)

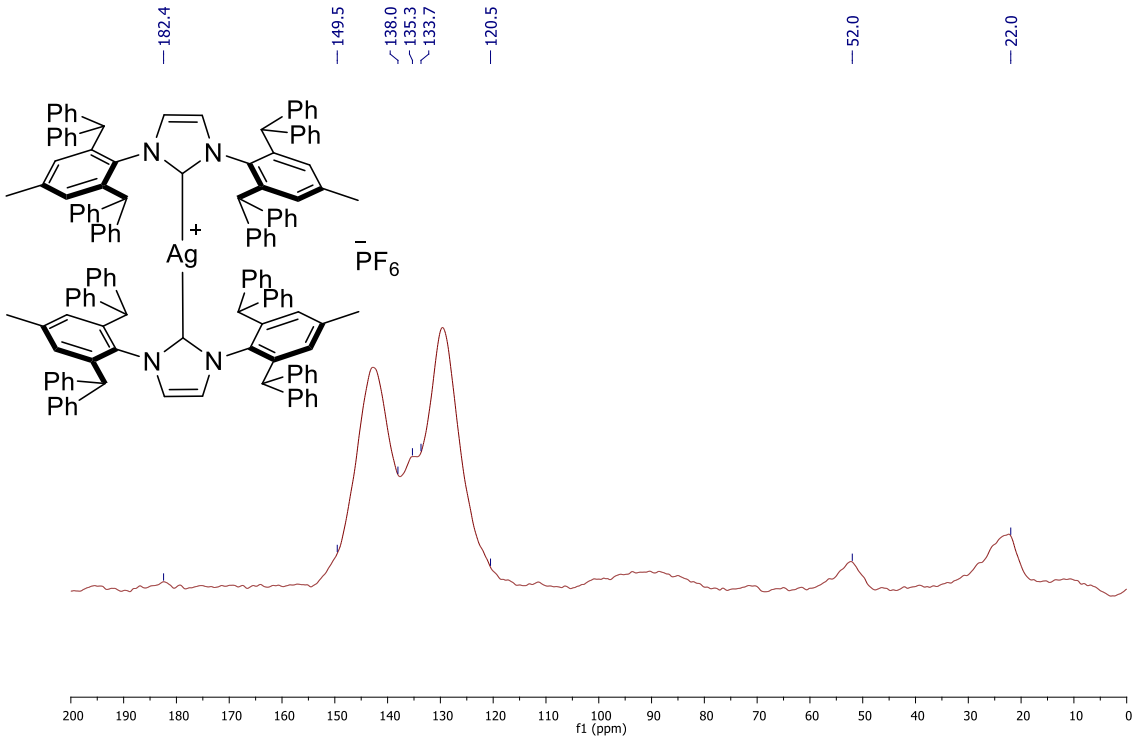


Bis[(1,3-bis(4-methyl-2,6-diphenyl)phenyl)imidazol-2-ylidene]silver hexafluorophosphate 4e

^{1}H solid state HR-MAS NMR (600 MHz)

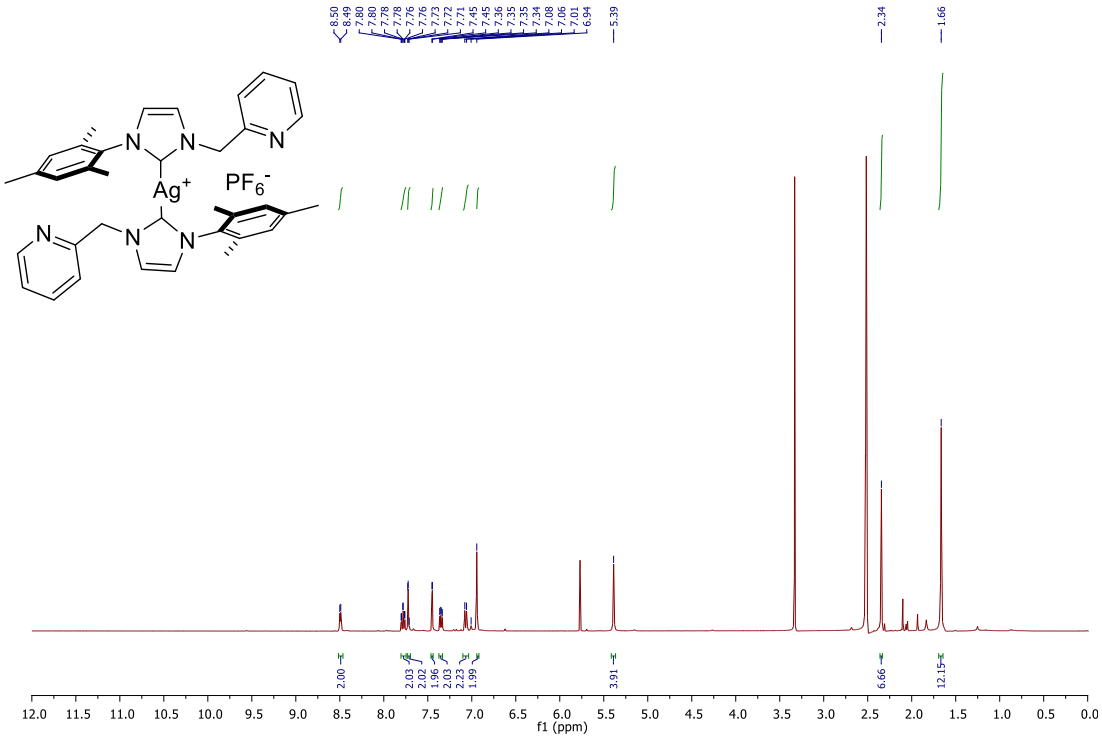


^{13}C solid state HR-MAS NMR (151 MHz)

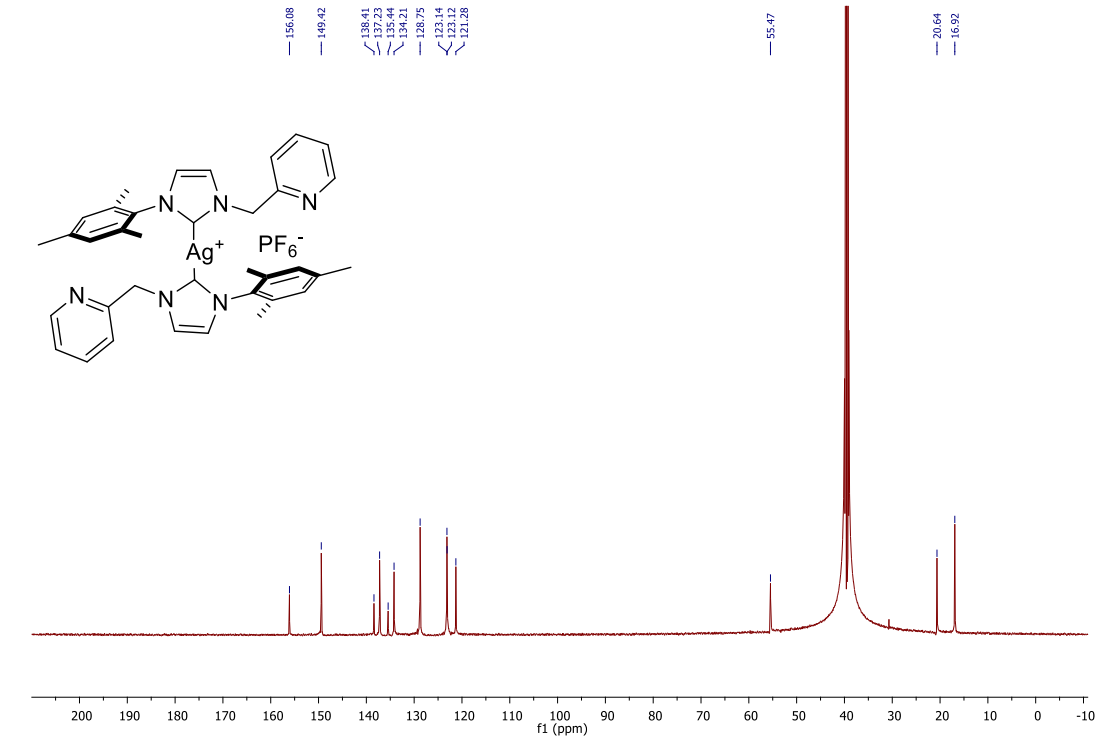


Bis[(1-(2-pyridyl)methylene-3-mesityl)imidazol-2-ylidene]silver hexafluorophosphate 4f

^{1}H NMR (400 MHz, DMSO-d_6)

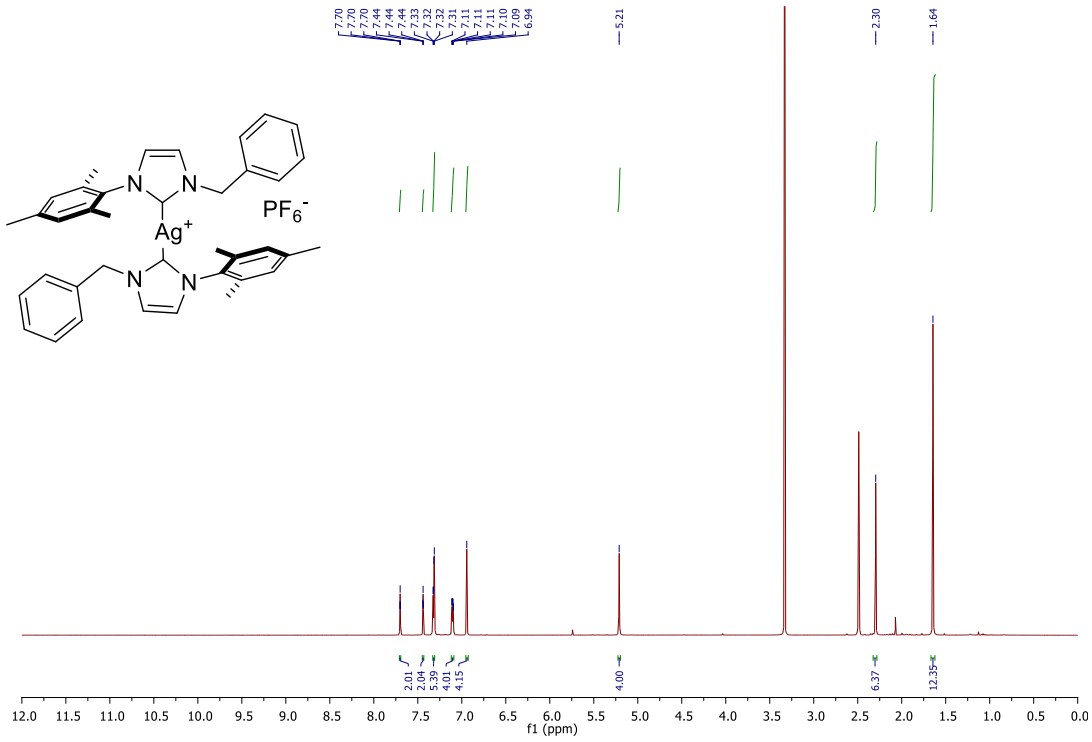


^{13}C NMR (151 MHz, DMSO-d_6)

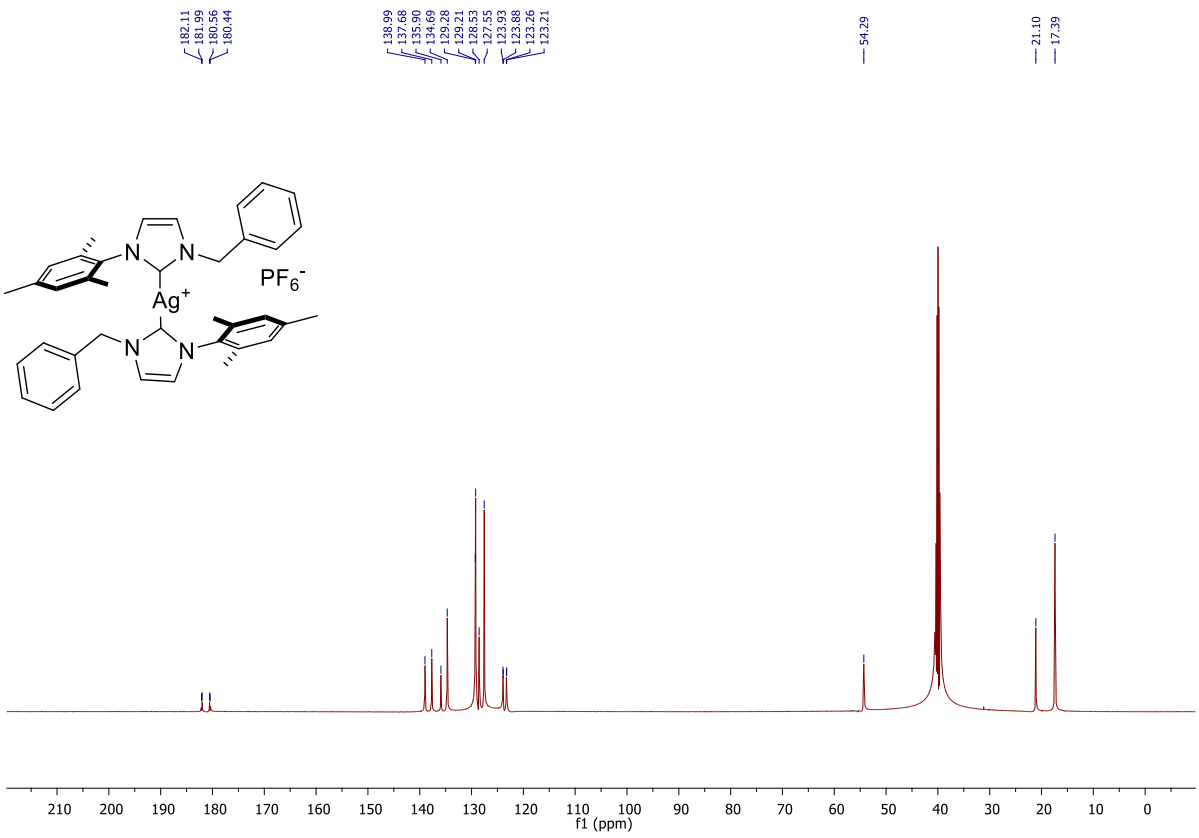


Bis[(1-benzyl-3-mesityl)imidazol-2-ylidene]silver hexafluorophosphate 4g

^{1}H NMR (500 MHz, DMSO-d_6)

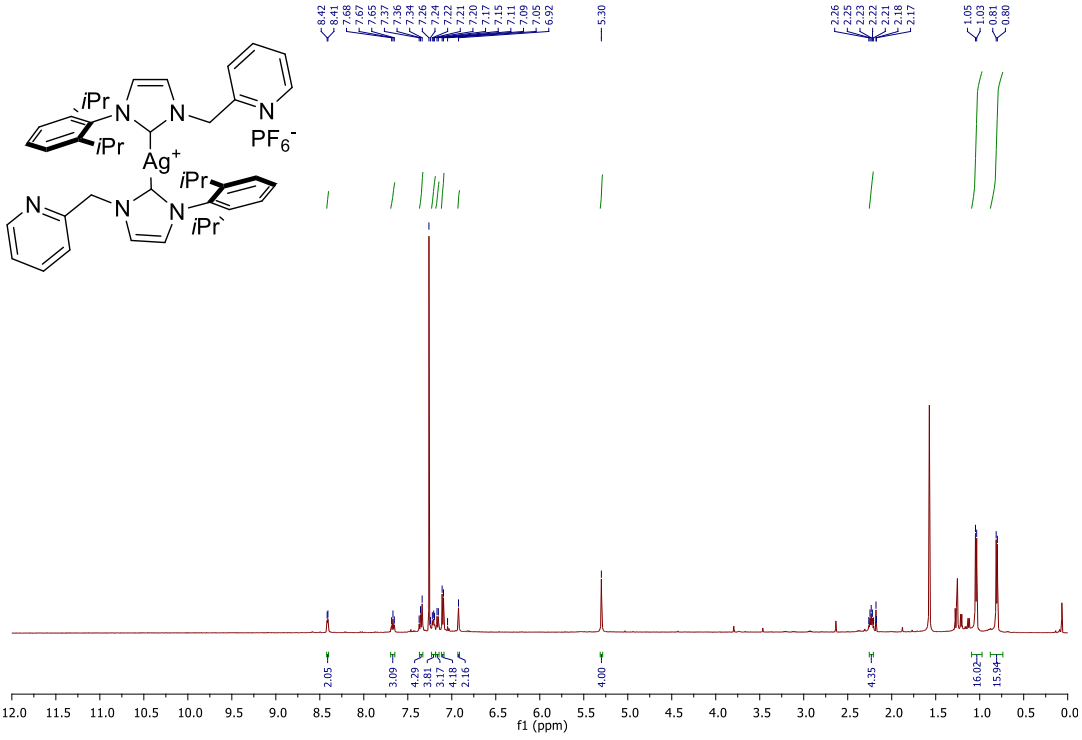


^{13}C NMR (126 MHz, DMSO-d_6)

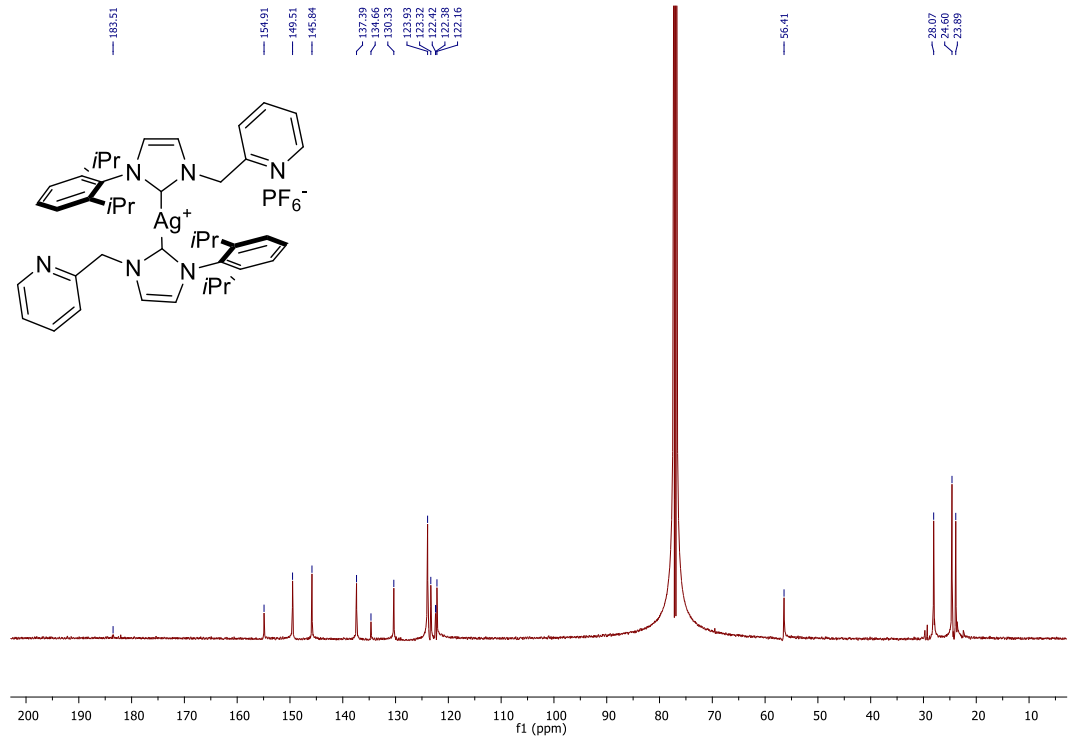


Bis[(1-(2-pyridyl)methylene-3-(2,6-diisopropylphenyl))imidazol-2-ylidene]silver hexafluorophosphate 4h

^{1}H NMR (500 MHz, $CDCl_3$)

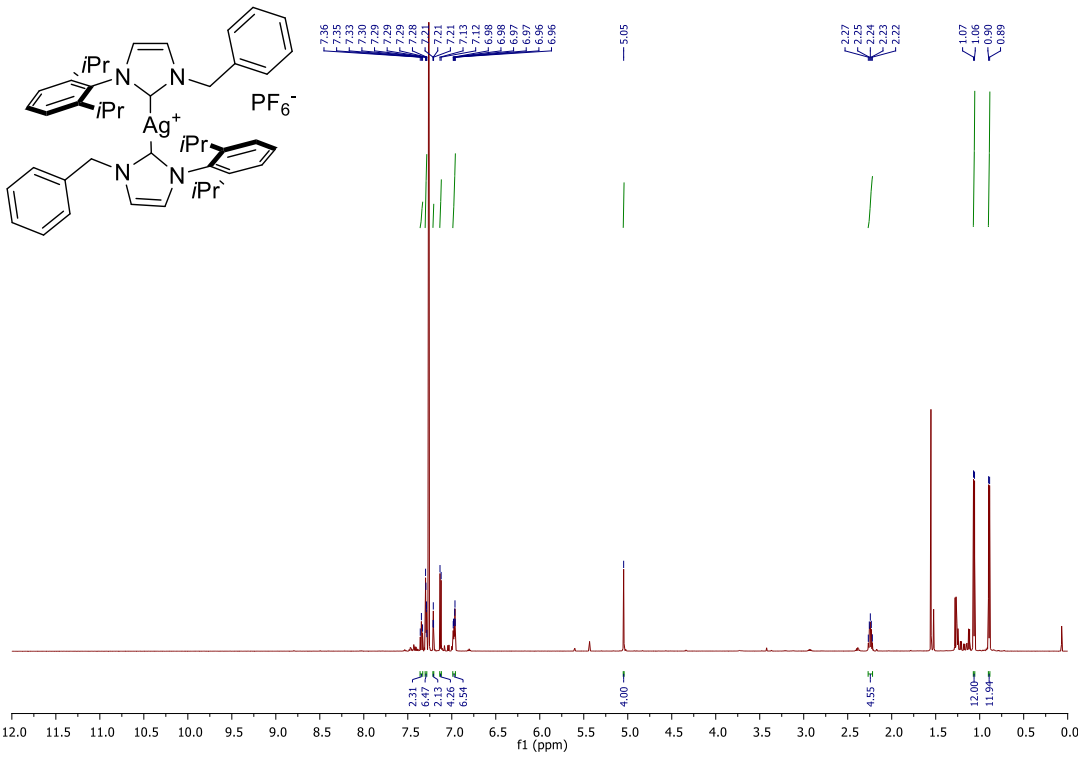


^{13}C NMR (126 MHz, $CDCl_3$)

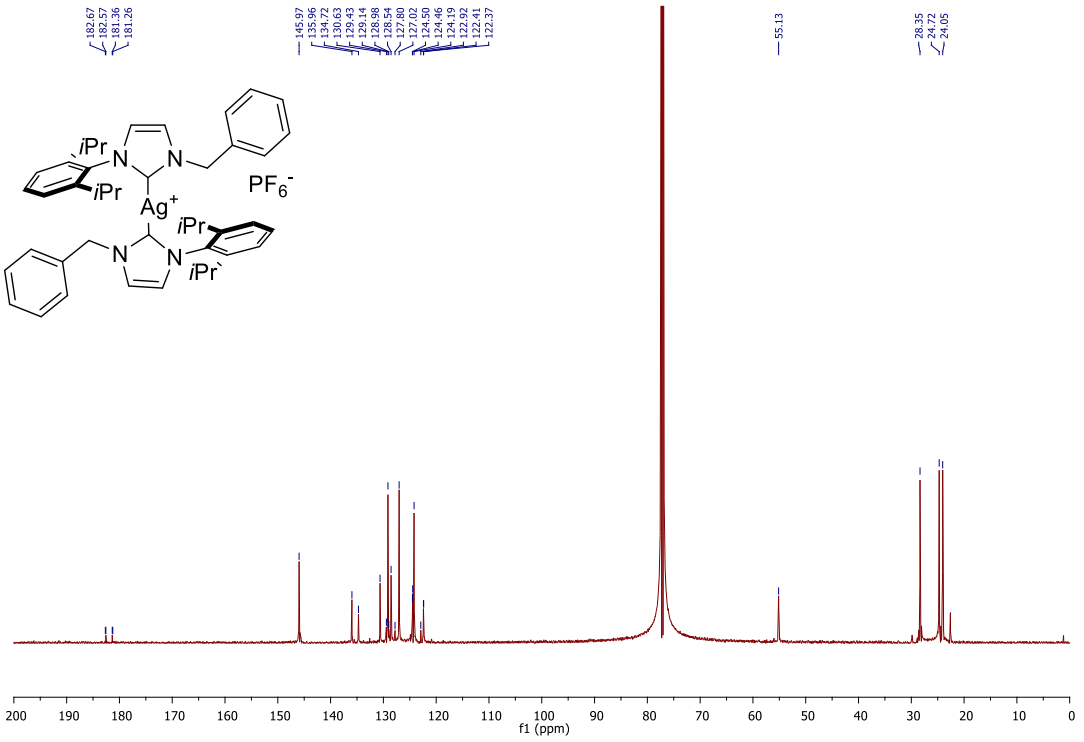


Bis[(1-benzyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene]silver hexafluorophosphate 4i

^{1}H NMR (600 MHz, $CDCl_3$)

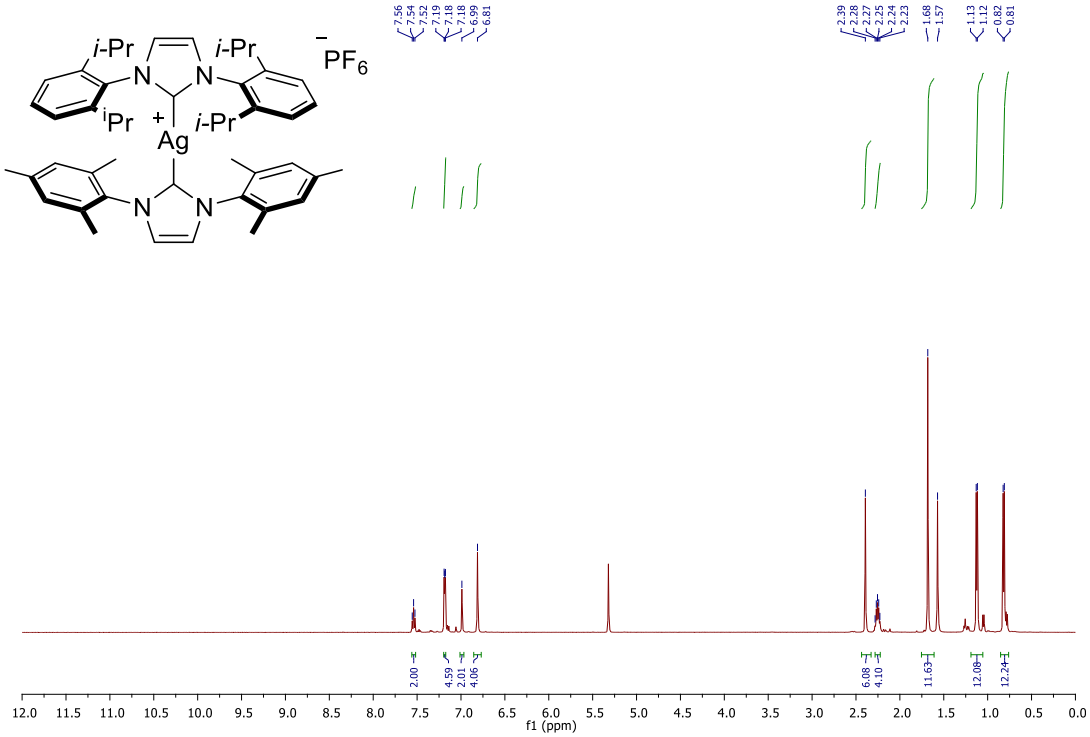


^{13}C NMR (151 MHz, $CDCl_3$)

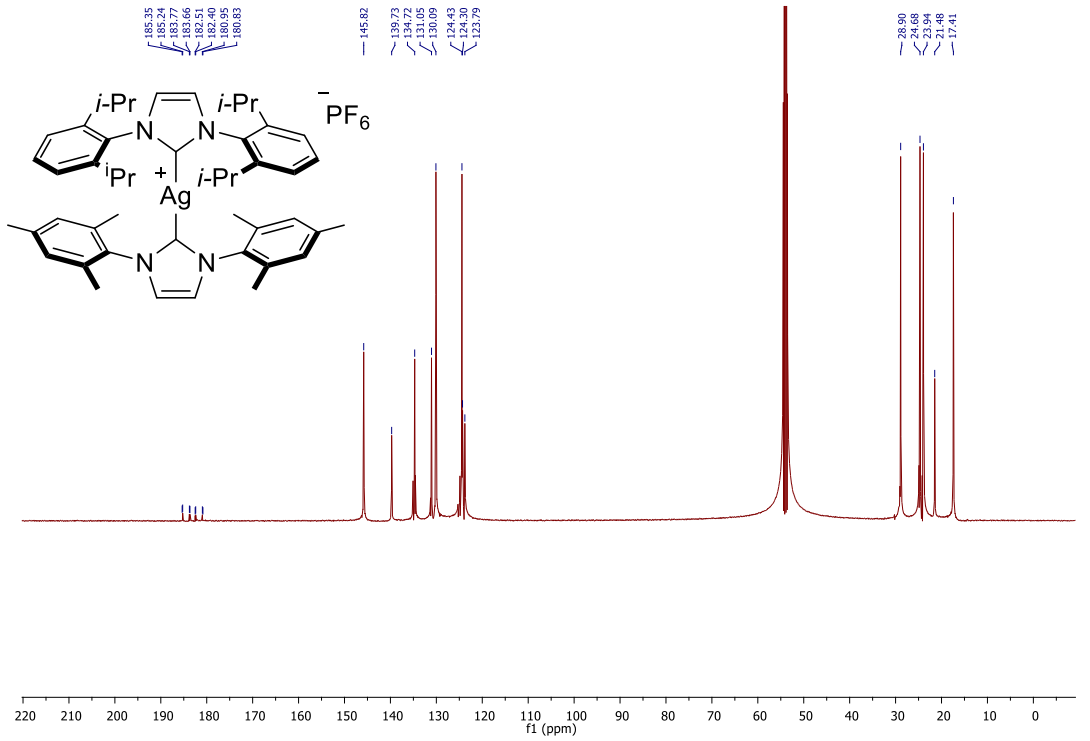


[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]silver chloride 5a

^{1}H NMR (500 MHz, CD_2Cl_2)

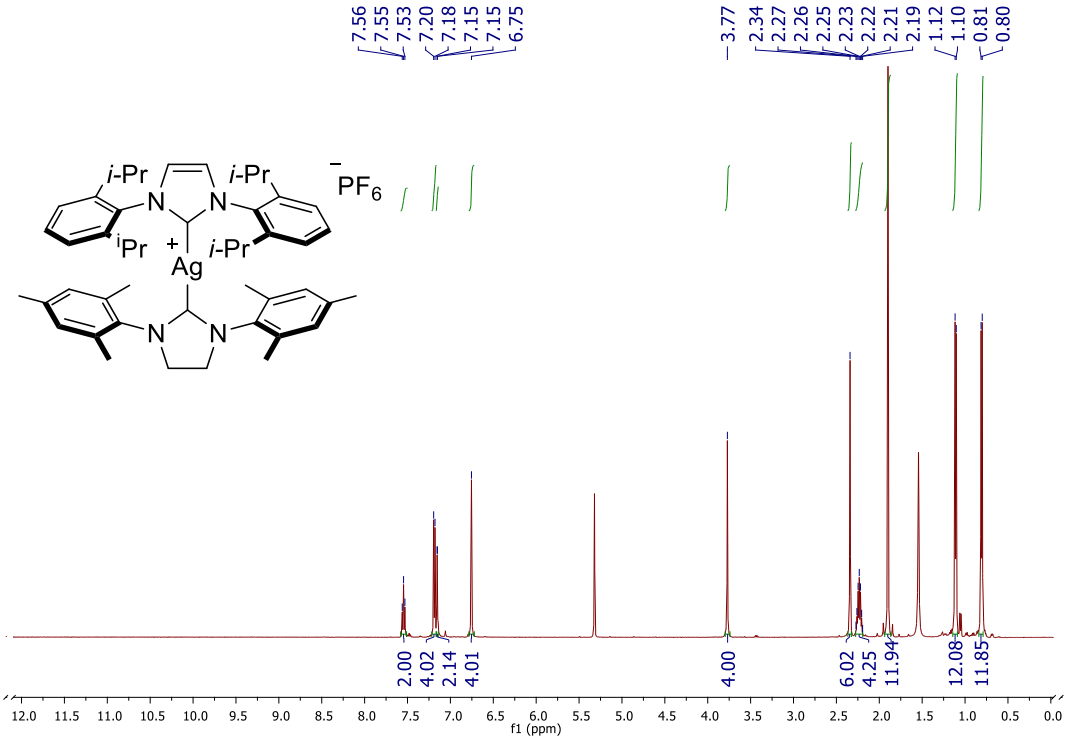


^{13}C NMR (126 MHz, CD_2Cl_2)

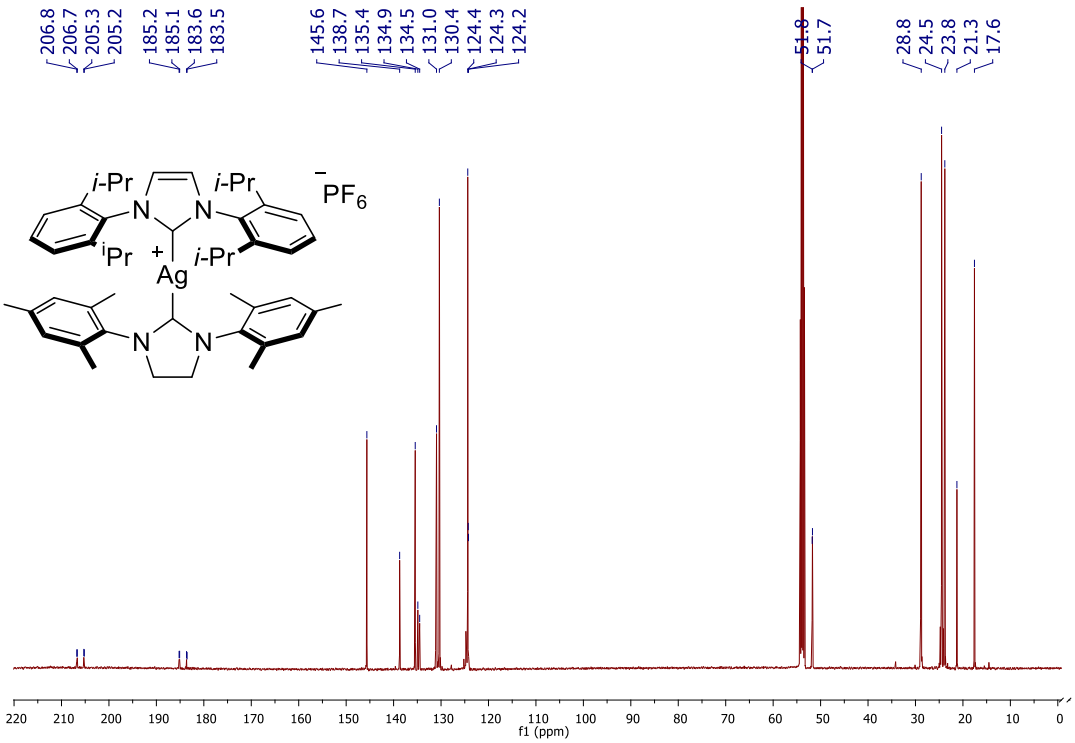


[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]silver chloride 5b

^{1}H NMR (500 MHz, CD_2Cl_2)

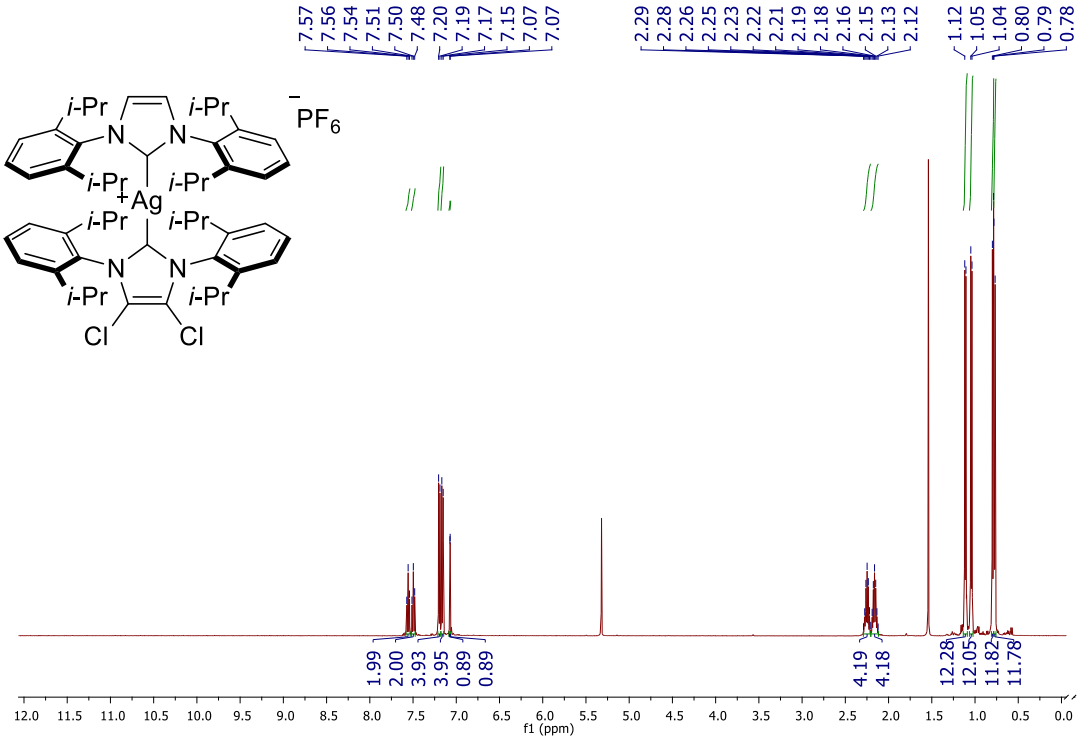


^{13}C NMR (126 MHz, CD_2Cl_2)

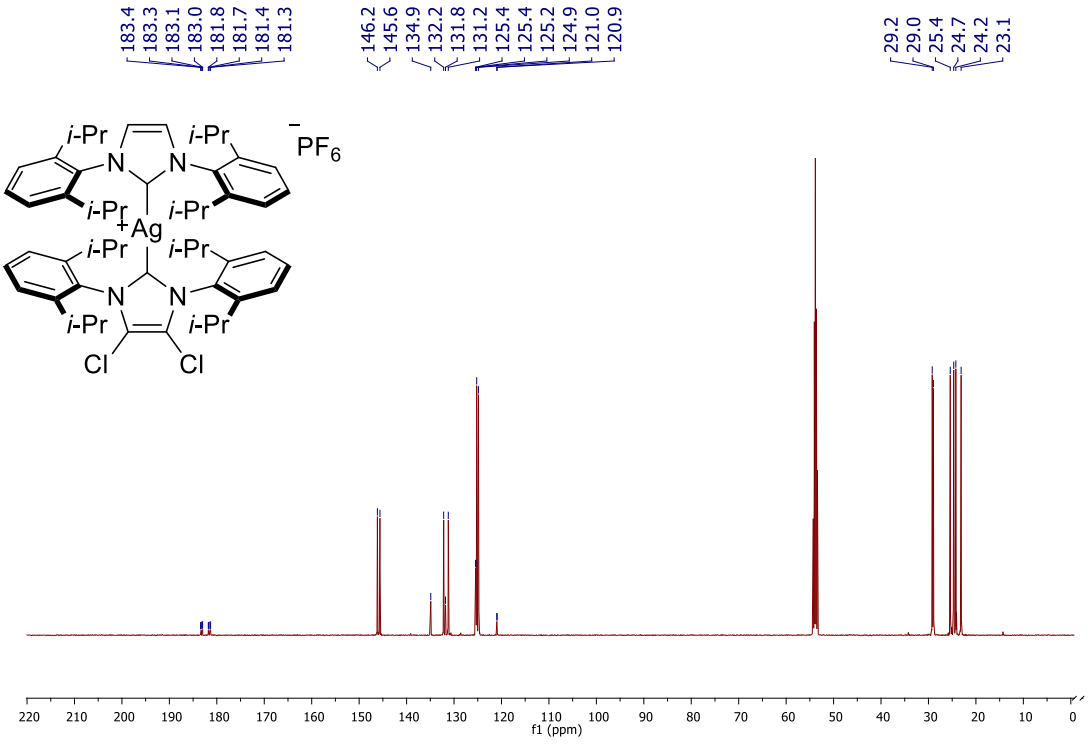


[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3-Bis(2,6-di*iso*propyl)phenyl]-4,5-dichloroimidazol-2-ylidene]silver hexafluorophosphate 5c

^{1}H NMR (500 MHz, CD_2Cl_2)

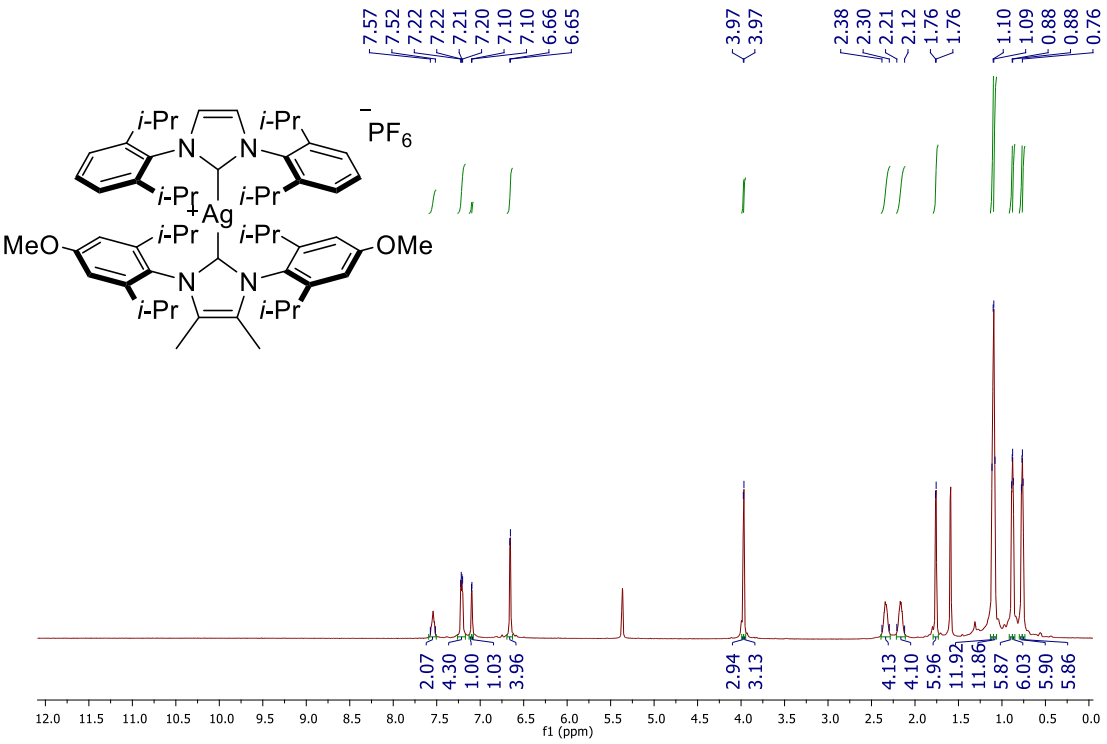


^{13}C NMR (126 MHz, CD_2Cl_2)

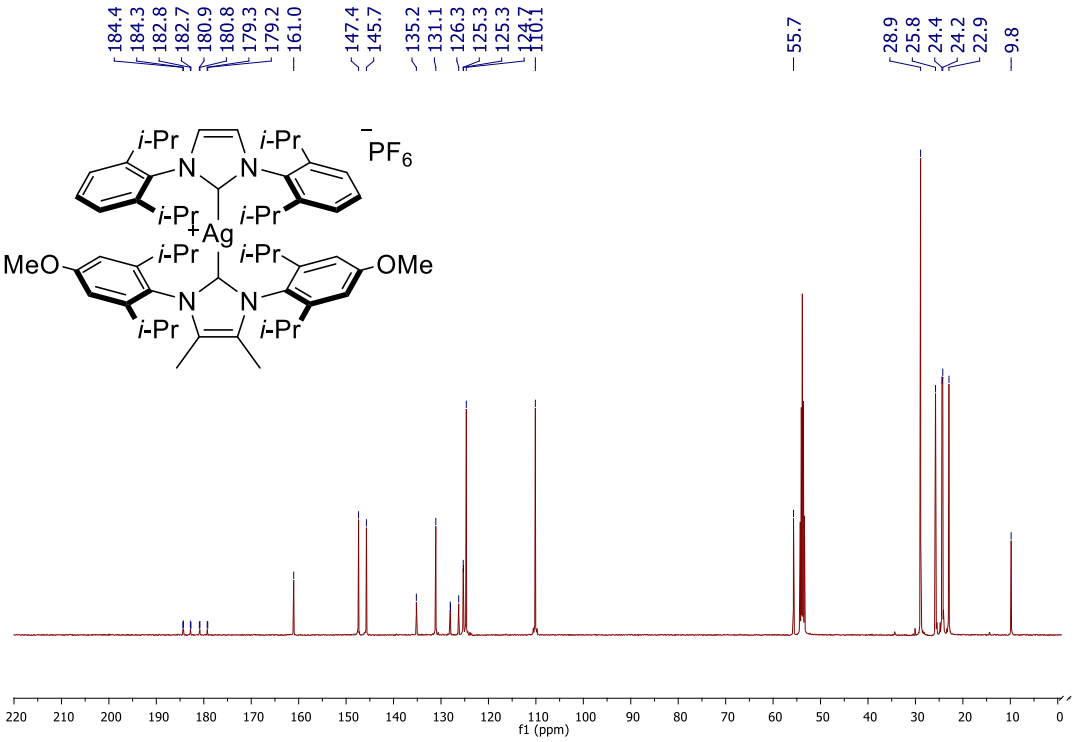


[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][(4,5-dimethyl-1,3-bis(4-methoxy-2,6-di*iso*propyl)phenyl)imidazol-2-ylidene]silver hexafluorophosphate 5d

^{1}H NMR (500 MHz, CD_2Cl_2)

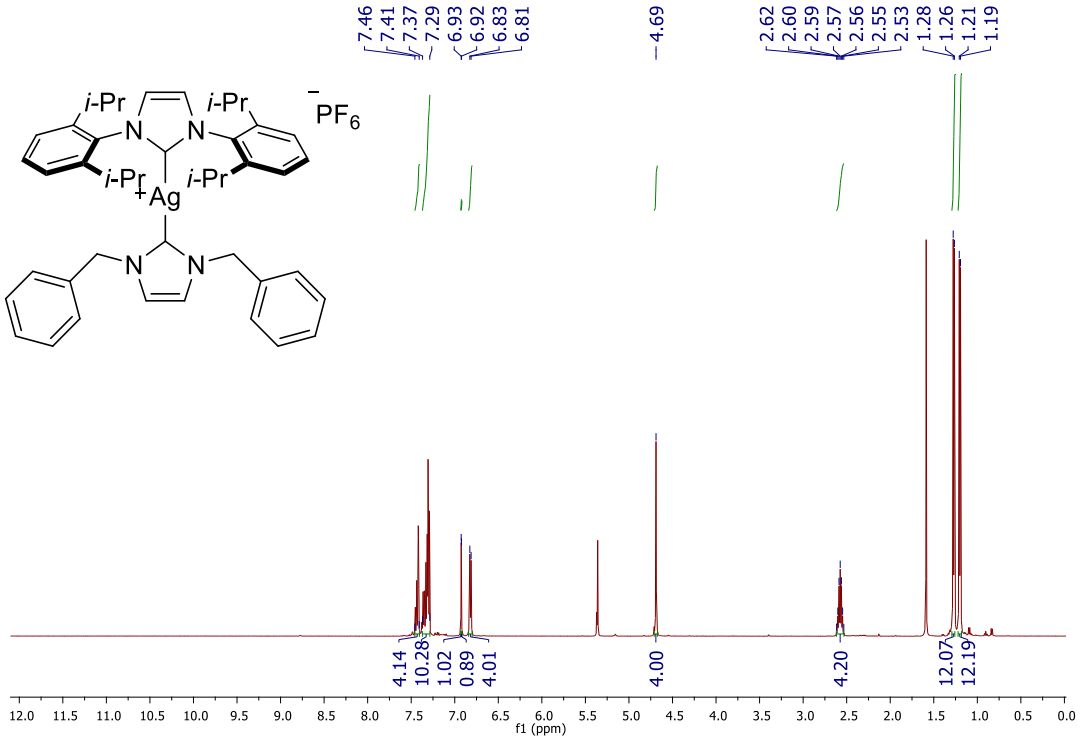


^{13}C NMR (126 MHz, CD_2Cl_2)

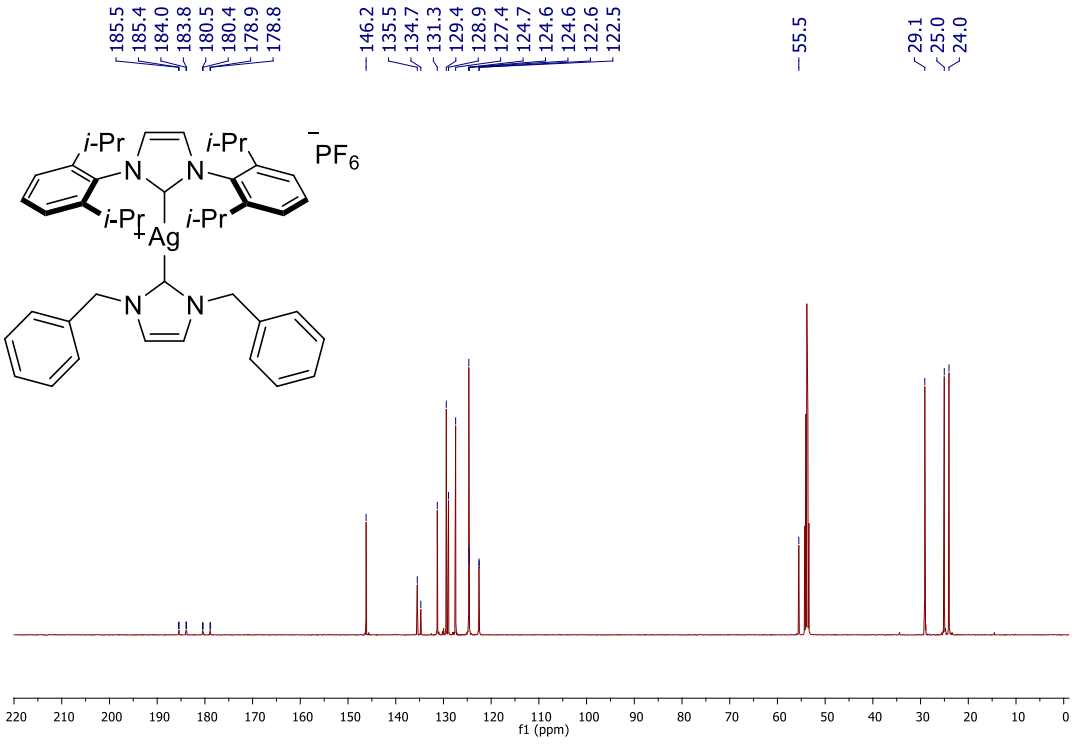


[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][*N,N*-dibenzylimidazolium]silver hexafluorophosphate 5e

^{1}H NMR (500 MHz, CD_2Cl_2)

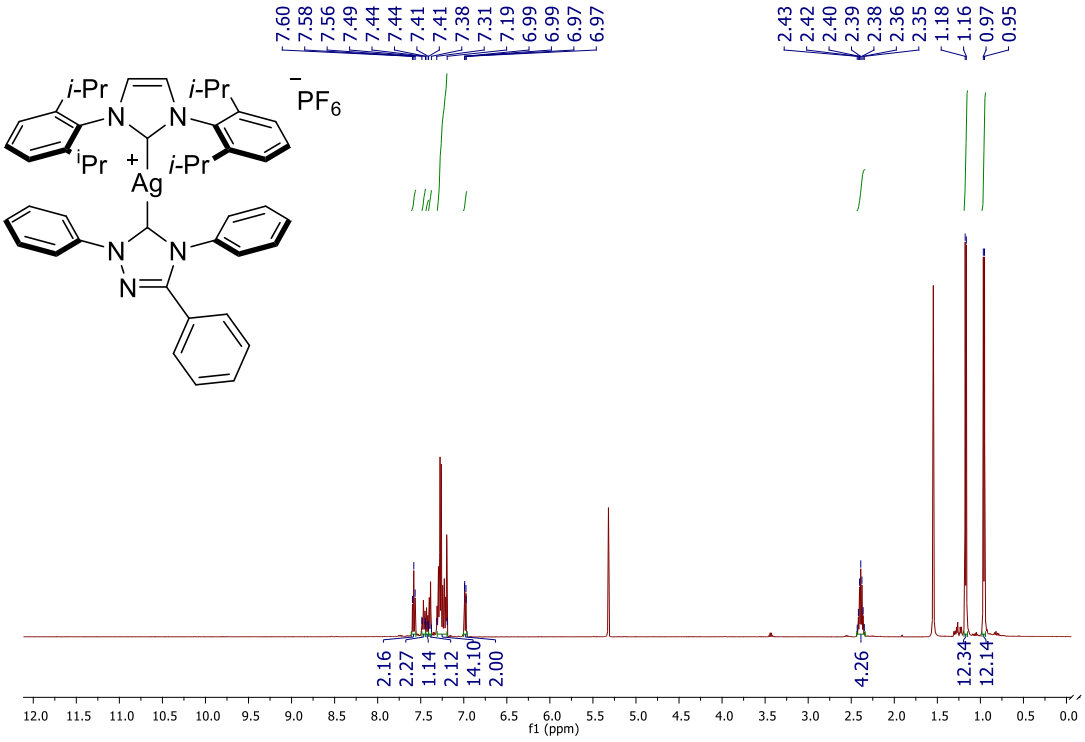


^{13}C NMR (126 MHz, CD_2Cl_2)

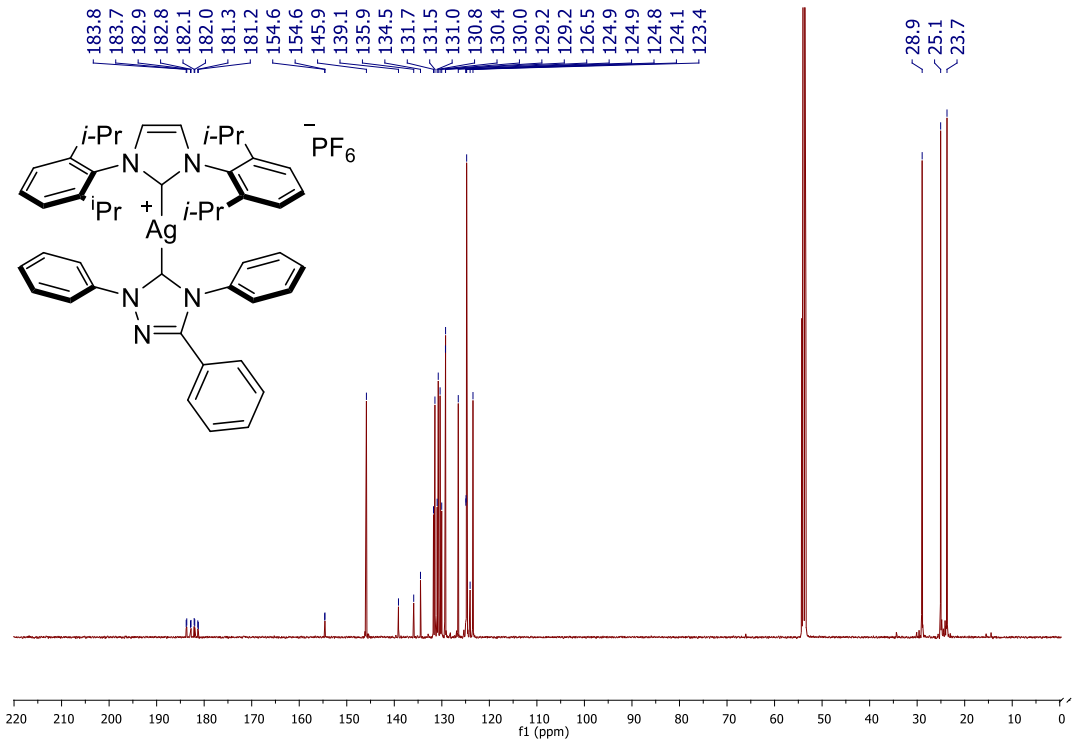


[[1,3-Bis(2,6-di*iso*propyl)phenyl]imidazol-2-ylidene][1,3,4-triphenyl-1,2,4-triazolium]silver hexafluorophosphate 5f

^{1}H NMR (500 MHz, CD_2Cl_2)



^{13}C NMR (126 MHz, CD_2Cl_2)



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